11:12:35 OCA PAD AMENDMENT - PROJECT HEADER INFORMATION 03/11/92

Active

Project #: E-19-639 Cost share #: Rev #: 9
Center # : 10/24-6-R6989-0A0 Center shr #: 10/22-1-F6989-0A0 OCA file #:
Work type : RES
Contract#: SK90A027 Mod #: SA03 Document : SUBCONT
Prime #: NAS8-36407 Contract entity: GTRC

Subprojects ? : N CFDA: N/A
Main project #: PE #: N/A

Project unit: CHEM ENGR Unit code: 02.010.114
Project director(s):
AGRAWAL P K CHEM ENGR (404)894-2826

Sponsor/division names: MCDONNELL DOUGLAS CORP / ST LOUIS, MO
Sponsor/division codes: 212 / 045

Award period: 900611 to 920331 (performance) 920331 (reports)

Sponsor amount	New this change	Total to date
Contract value	0.00	178,954.37
Funded	0.00	178,954.37
Cost sharing amount		0.00

Does subcontracting plan apply ?: N

Title: A KINETIC STUDY OF THE BOSCH REACTION

PROJECT ADMINISTRATION DATA

OCA contact: Ina R. Lashley 894-4820

Sponsor technical contact

MR ROBERT DALEE
(205)922-7320

Sponsor issuing office

DANIEL E BEGGS, BUYER
(205)922-7503

MCDONNELL DOUGLAS SPACE SYSTEMS CO
HUNTSVILLE DIVISION
689 DISCOVERY DRIVE
HUNTSVILLE, ALABAMA 35806

Security class (U,C,S,TS) : U ONR resident rep. is ACO (Y/N): N
Defense priority rating : DO-C9 N/A supplemental sheet
Equipment title vests with: Sponsor GIT X
<$5K W/APPROVAL VESTS W/TECH; >$5K MAY VEST W/TECH.(PER FAR 52-245.5 ALT I).
Administrative comments -
SUPPLEMENT 03 GRANTS A NO-COST EXTENSION TO 3/31/92, AS REQUESTED IN LETTER DATED 1/15/92.

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

512.7552.

Closeout Notice Date 08/12/93
Original Closeout Started 08/02/91

Project No. E-19-639 Center No. 10/24-6-R6989-0A0

Project Director AGRAWAL P K School/Lab CHEM ENGR

Sponsor MCDONNELL DOUGLAS CORP/ST LOUIS, MO

Contract/Grant No. SK90A027 Contract Entity GTRC

Prime Contract No. NAS8-36407

Title A KINETIC STUDY OF THE BOSCH REACTION

Effective Completion Date 920331 (Performance) 920430 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	Y	920925
Final Report of Inventions and/or Subcontracts	Y	920131
Government Property Inventory & Related Certificate	Y	920128
Classified Material Certificate	N	
Release and Assignment	Y	
Other	N	

CommentsEFFECTIVE DATE 6-11-90. CONTRACT VALUE $178,954.37.

Subproject Under Main Project No.

Continues Project No.

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Managment	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other CARL BAXTER-FMD	Y
FRED CAIN-OOD	Y

* Note: Final Patent Questionnaire sent to PDPI.

Ms. Robin McElyea
McDonnell Douglas Space Systems
Huntsville Division
689 Discovery Drive
Huntsville, AL 35806

September 7,1990

SUBJECT : Monthly Progress Reports/ Subcontract SK90A027

Dear Ms. McElyea :

Please find enclosed a copy of the monthly progress reports for the above subcontract, for the months of July,1990 and August,1990. Please call me at (404) 894-2826 if you have any questions or if you would prefer a different format for these reports in the future.

With best wishes.

Sincerely Yours'

cc: enclosed (2)

Pradeep K. Agrawal
Associate Professor

Progress Report (Subcontract SK90A027) Period : July-August,1990

The following tasks were carried out :

(1) A computer model to investigate the different regions of operating conditions (temperature, feed composition) has been almost completed. It has not been tested yet. The purpose of this model would be to identify the operating conditions where the thermodynamics for the Bosch Reaction are unfavorable ; these conditions would be avoided in our reactor studies.

(2) The design for the reactor system has been completed. All the parts needed for the reactor have been ordered. Most parts have been received by now, and the raector set up is almost complete. We expect the reactor to be ready for testing by the end of september,1990.

(3) The gas chromatograph for the analysis of reactor inlet and effluent streams has been set up. We have tested two different GC column packings and found that Carbosieve S will be suitable for separating all the components that we wish to analyze for using our GC. The GC column has been ready. We are waiting for the certified grade mixture of the gases for the GC calibration and this component should be ready by the september,1990. At that time, the reactant gas supply (ultra high purity grade) should also be ready. Thus the stage is set to begin reactor studies by the end of September,1990. So far, our progress is on schedule, as planned.

Georgia Institute of Technology
School of Chemical Engineering
Atlanta, Georgia 30332-0100
FAX (404) 894- 2866
(404) 894-

DESIGNING TOMORROW TODAY

October 11, 1990

Ms. Robin McElyea
McDonnell Douglas Space Systems
Huntsville Division
689 Discovery Drive
Huntsville, GA 35806

RE: Monthly Progress Report/Subcontract SK90A027

Dear Ms. McElyea:

Please find enclosed a copy of the monthly progress report for the above subcontract, for the month of September, 1990.

Please call me at (404) 894-2826 if you have any questions.

Sincerely yours,

Pradeep K. Agrawal
Associate Professor

PKA/srj

encl.

SUBCONTRACT # SK90A027
Monthly Progress Report (September, 1990)

The following tasks were carried out:

(1) The reactor set up has been completed. This includes the temperature control of the catalyst bed, flow lines for the reactor inlet and outlet, and installation of an on-line GC. The flow lines (one eighth inch diameter stainless steel tube) have been tested and fixed for any leaks.

(2) The Carbosieve S GC column packing has been chosen and tested for the separation of CO, CO_2, CH_4, and H_2O. The calibration of the GC is currently in progress. The column operating conditions have been optimized for proper separation of all gas-phase components.

December 7, 1990

Ms. Robin McElyea
McDonnell Douglas Space Systems
Huntsville Division
689 Discovery Drive
Huntsville, AL 35806

RE: Monthly Progress Report/Subcontract SK90A027

Dear Ms. McElyea:

Please find enclosed a copy of the monthly progress reports for the above subcontract, for the month of November, 1990.

Please call me at (404) 894-2826 if you have any questions.

Sincerely,

Pradeep K. Agrawal
Associate Professor

PKA/srj

Enclosures

Progress Report (Subcontract SK90A027) November, 1990

This month has been most productive in terms of our reactor operation. Preliminary reaction studies were begun using Ni/SiO_2 catalysts at temperatures between 400°C and 600°C. The feed consisted of 10% CO_2, 20% H_2, and balance He. The reactor effluent was analyzed using on-stream GC. The results can be summarized as below:

(1) At each of the three temperatures (400°C, 500°C, and 600°C), there is very little (less than 5%) loss in catalytic activity even after 10-20 hour of operation. This is very encouraging, since in iron one would expect severe activity drop within the first 3-4 hour of operation. We believe it to be due to the thermodynamic instability of nickel carbide at these temperatures.

(2) Methane and water are the major reaction products at 400°C, with only a small amount of carbon monoxide being present. However, at 600°C, carbon monoxide is the major reaction product, and very little methane is present. This result is as I would expect it to be. At elevated temperatures, CO adsorption on nickel is thermodynamically inhibited, thus preventing methane formation. Hence, any CO formed via reverse water gas shift reaction would desorb instead of participation in the Boudouard reaction or methanation reaction.

We continue to work with this nickel catalyst and other nickel and iron catalysts. Our first task is to establish the reproducibility of these results as well as to define the behavior of blank reactor.

Georgia Institute of Technology
Polymer Education & Research Center
Atlanta, Georgia 30332-
(404) 894-2826

DESIGNING TOMORROW TODAY

January 10,1991

Ms. Robin McElyea
McDonnell Douglas Space Systems
Huntsville Division
689 Discovery Drive
Huntsville, AL 35806

RE: Monthly Progress Report/Subcontract SK90A027

Dear Ms. McElyea:

Please find enclosed a copy of the monthly progress reports for the above subcontract, for the month of December, 1990.

Please call me at (404) 894-2826 if you have any questions.

Sincerely,

Pradeep K. Agrawal
Associate Professor

PKA/srj

Enclosures

Progress Report (Subcontract SK90A027) December,1990

After successfully initiating the reactor studies in November,1990, we bagan experiments on the rector to establish the baseline behavior (i.e. the catalytic activity of the blank rector) at several temperatures in the range of our experiments. We also began the task of checking the reproducibility of the reactor results obtained in November,1990. The results are summarized below :

(1) The catalytic activity of the Ni/SiO_2 is entirely reproducible over the temperature range of 400 °C to 700 °C . The production of CO is enhanced at temperatures above 500 °C whereas the production of methane and water dominates at lower temperatures.

(2) The blank reactor had non-negligible activity for the above reaction at these temperatures. After careful and sequential removal of each possible cause of this blank reactor activity, it was finally determined that the background activity is caused by the metals deposited on the reactor stainless steel walls. The feed tank contains nickel carbonyls and iron carbonyls (compounds that are gaseous at room temperature but decompose at temperatures above 150 C. Thus , the deposition of Ni and Fe on the stainless steel rector walls cause the baseline activity. We were successful in removing these metals by treating the reactor with aqua regia, however, after a few runs the metal deposition again became problemsome. We have therefore, resolved this problem by putting a heated (to 175 C) bed of neutral alumina in the feed line containing the carbonyls. These carbonyls will be decomposed over the alumina bed, while contributing negligible activity towards the Bosch reaction at 175 C. This has been accomplished now and should alleviate the baseline activity problem.

There has been a breakdown of our gas chromatograph, and the repairs are going to be needed. We have already done the paperwork needed to proceed with the repairs (to be done by the GC manufacturer Hewlett-Packard), and have been able to borrow another GC from another lab in the School of Chemical Engineering. Currently, we are working to put this GC into operation to make progress on our reactor studies.

Georgia Institute of Technology
School of Chemical Engineering
Atlanta, Georgia 30332-0100
FAX (404) 894-2866
(404) 894-2826

DESIGNING TOMORROW TODAY

March 20, 1991

Ms. Robin McElyea
McDonnell Douglas Space Systems
Huntsville Division
689 Discovery Drive
Huntsville, Alabama 35806

RE: Monthly Progress Report/Subcontract SK90A027

Dear Ms. McElyea:

I am sorry for the delay in mailing you the monthly progress report for February, 1991. The same is enclosed herewith for your records. Please call me at (404) 894-2826 if you have any questions.

Thank you.

Sincerely,

Pradeep K. Agrawal
Associate Professor

PKA/sg
Enclosures

Progress Report (Subcontract SK90A027) February, 1991

We had lost the month of January, 1991 entirely in terms of reactor studies, due to the breakdown of GC. The GC was fully operational (a new unit) at the end of January, 1991. While trying to fix the GC problems, efforts were devoted towards thermodynamic calculations as well. Below are the key results, obtained in February, 1991:

1. The reactor operation is going smoothly. Presently, the work has continued entirely with the CO_2/H_2 feed only and Ni/SiO_2 catalyst has been employed. The gas mixtures have been ordered to employ the feed containing methane and carbon monoxide (for kinetic modeling). A major improvement in reactor operation was achieved by replacing stainless steel reactor with the copper tube reactor. This new reactor gives background activity for the Bosch reaction which is an order of magnitude lower than that observed with the stainless steel reactor. This is significant in that we will be able to measure quantitatively the activity of catalyst employed. We are getting ready to start using Fe/SiO_2 catalysts for our reactor studies.

2. X-ray diffraction and SEM studies have been initiated with the Ni/SiO_2 catalysts.

3. Thermodynamic modeling of the C-H-O system has been completed. The effect of several parameters, e.g., temperature, no. of moles of $H_2O(\alpha)$, $CO_2(B)$, and CH_4 $(1-\alpha-\beta)$ in the reactant feed, is being investigated using this model. The amount of solid carbon deposited during the reaction is also computed. We have just acquired a software package to obtain equilibrium curves on C-H-O ternary diagram.

Georgia Institute of Technology
School of Chemical Engineering
Atlanta, Georgia 30332-0100
FAX (404) 894-2866
(404) 894-2826

DESIGNING TOMORROW TODAY

May 14, 1991

Ms. Robin McElyea
McDonnell Douglas Space Systems
Huntsville Division
689 Discovery Drive
Huntsville, Alabama 35806

RE: Monthly Progress Report/Subcontract SK90A027

Dear Ms. McElyea:

Please find enclosed the progress report combined for the month of April, 1991. Feel free to call me if you have any questions.

Best regards.

Sincerely,

Pardeep K. Agrawal
Associate Professor

PKA/sg
Enclosure
cc: Mr. Bob Dalee
Ms. Robyn Carrasquillo

Progress Report (Subcontract SK 90A027) April, 1991

The studies conducted during this month have included the (i) Reactor Studies, (ii) SEM studies of used and Fresh Catalysts, and (iii) x-ray diffraction studies. I was given some samples of spent iron catalysts (from Life Systems, Inc.) during my visit to Huntsville, Alabama in November, 1990. One of these samples was examined using XRD and SEM; the results are summarized below.

Reactor Studies

The entire month of April, 1991 was spent on studying $Fe/\nu-Al_2O_3$ commercial catalyst using 10%CO_2/20% H_2/balance He feed. Three different reactor runs were made using iron catalyst from the same batch. In each case, the fresh loaded catalysts were in-situ oxidized in O_2/He mixture at 400°C for 2-3 hours. This oxidation pretreatment was followed by reduction in H_2 at 500°C for 6 hours and then at 600°C for another 4-8 hours. The oxidation-reduction pretreatment was used to remove any carbon from the catalyst and more importantly to ensure similar initial activity state for each catalyst.

The first run was begun at 400°C. After 140 hours of operation, the reaction temperature was increased to 500°C. After about 60 hours of 500°C operation the temperature was reduced to 400°C for another 60 hour operation. This was followed by another 500°C operation followed by 600°C operation. The catalyst activity for CO formation is shown in Figure 1 (the raw data are shown in Table 1). This run was carried out for a total of 11-12 days. The rate of methanation was very small, as would be expected. The main features of the results are highlighted below. Surprisingly, the catalytic activity increased during the initial 400°C operation. After 3 days of operation the activity had doubled which then stabilized. This observation is somewhat surprising in that the activity increased rather than decreased. As is discussed in the SEM results section, we attribute this increased to a faceting or restructuring of Fe catalyst surface which would increase the catalyst surface area. The constant activity thereafter indicates a lack of catalyst deactivation. Increasing the temperature up to 500°C didn't cause any significant deactivation. However, 600°C reactor operation caused catalyst deactivation. SEM also showed a lack of carbon fiber formation. We believe that deactivation is due to amorphous carbon or graphite deposits.

Second reactor run with iron catalyst was started after similar pretreatment, but the reaction was begun at 600°C (without a 400°C operation). In this run, no activity increase was observed (as was observed in first run 400°C operation). The catalyst activity decreased by approximately a factor of two after 5 days of operation. Most of the decrease was observed during the first two days of operation after which the rate of catalyst deactivation slowed considerably. During the last 3 days of operation, there was only a ~10-12% activity decrease. This run was terminated due to a minor reactor problem.

The third reactor run was made with conditions identical to the second run (600°C), and the results for CO activity are summarized in Figure 2. This run was discontinued after 12 days of operation, and the samples were removed for SEM and

XRD characterization.

SEM Studies

For each of the iron catalysts studied above, SEM showed no evidence of carbon fiber formation. We had examined a sample of spent Fe catalyst (Life Systems, Inc.) which clearly showed the presence of carbon fibers. In all the used catalysts in our studies, there was a marked increase in the surface roughness caused presumably by breaking up of iron particles.

XRD Studies

XRD of "Life Systems" sample showed a predominance of graphite peak.

Figure 1

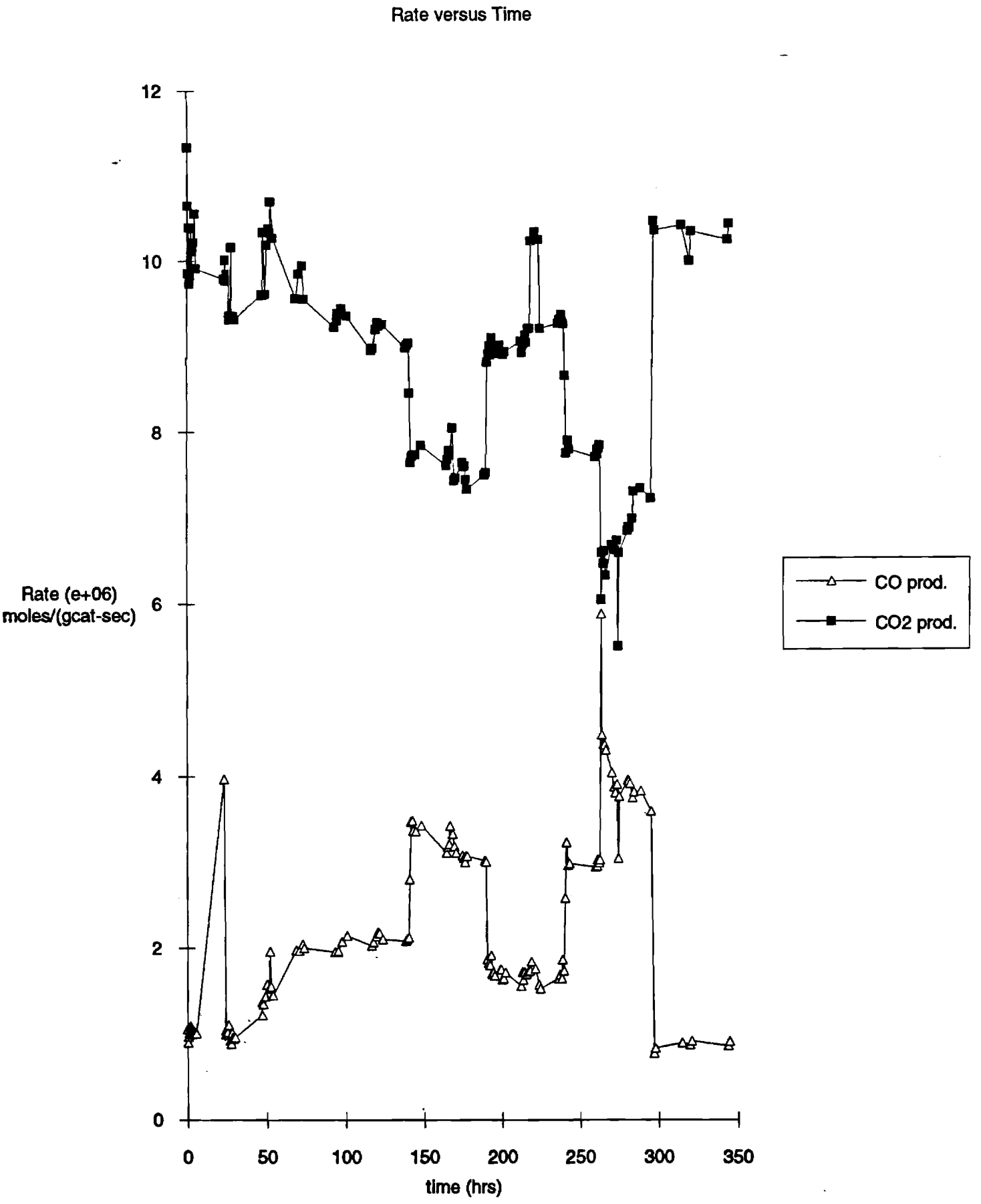

Rate versus Time
Rate (e+06) moles/(gcat-sec)
12
10
8
6
4
2
0
0
50
100
150
200
250
300
350
time (hrs)
CO prod.
CO2 prod.

Figure 2

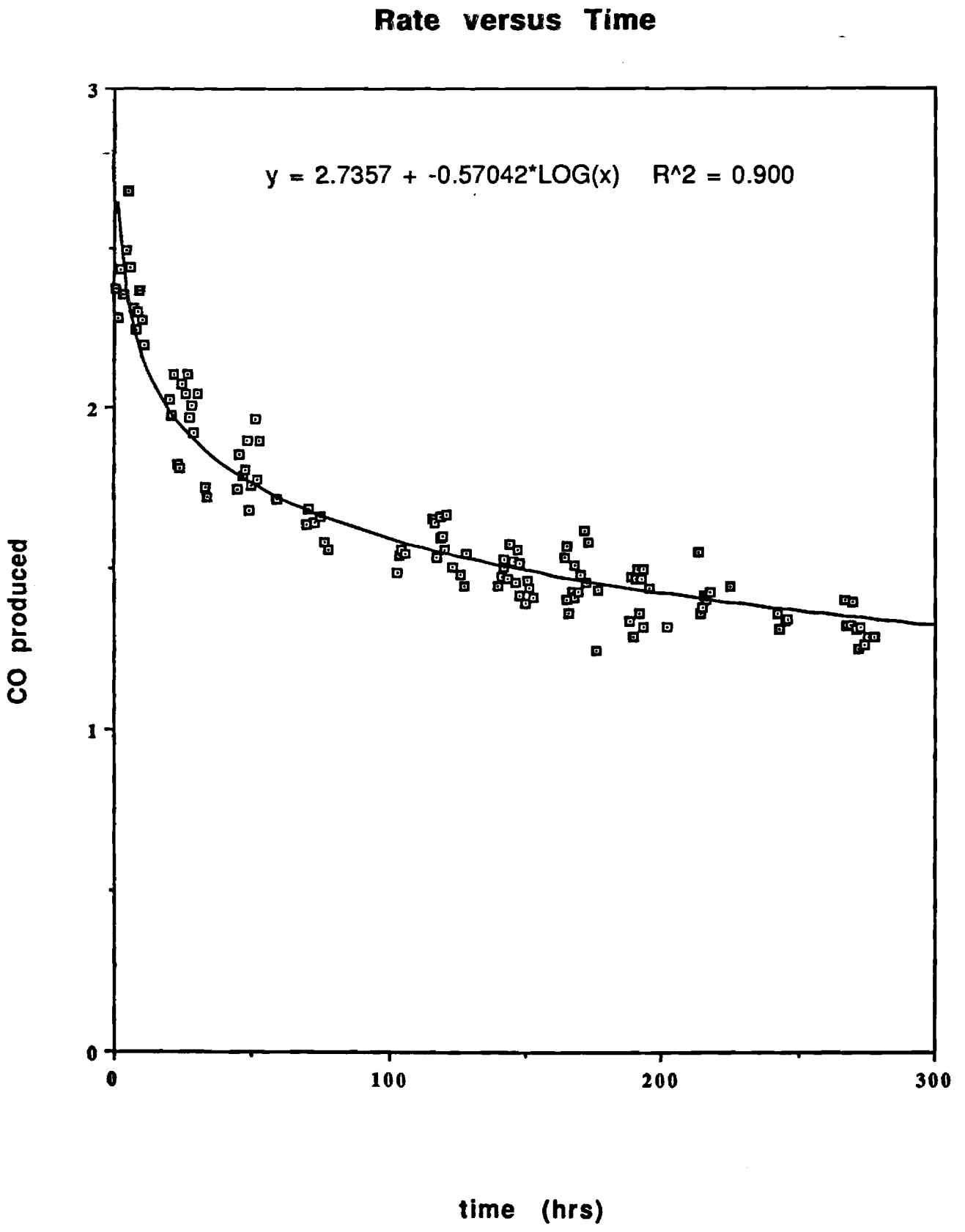

Rate versus Time
y = 2.7357 + -0.57042*LOG(x) R^2 = 0.900
CO produced
time (hrs)
0
1
2
3
0
100
200
300

TABLE I

changed 22400 cm³/mole to 24466.2 cm³/mole
0°C 25°C

Iron Catalyst Run @ 400 and 500 C

actual time	total time	rate cc	flow time (s)	Q cc / min	Areas CO	CO2	CH4	Aco+Aco2	Produced (g-mole/g-cat-s) CO	CO2	CH4	C	
3/30/91 14:36	0	10	14	42.8571	16085	192520	68	208605	1.041	10.863	0.006	-0.892637	
3/30/91 14:55	0.0131944	10	14	42.8571	13770	180626	224	194596	0.891	10.203	0.019	-0.096211	
3/30/91 15:25	0.0340278	10	15	40	15841	179344	499	195185	0.957	9.445	0.039	-0.158551	
3/30/91 15:57	0.05625	10	15	40	16486	189036	551	205522	0.996	9.955	0.044	-0.712028	
3/30/91 16:17	0.0701389	10	15	40	17769	177154	622	194923	1.073	9.330	0.049	-0.169374	
3/30/91 16:45	0.0895833	10	15	40	17158	178975	517	196133	1.036	9.425	0.041	-0.220078	
3/30/91 17:17	0.1118056	10	15	40	16795	188905	524	205700	1.014	9.948	0.041	-0.721657	
3/30/91 17:37	0.1256944	10	15	40	16290	180413	569	196703	0.984	9.501	0.045	-0.247496	
3/30/91 18:08	0.1472222	10	15	40	16983	183993	521	200976	1.026	9.690	0.041	-0.474091	
3/30/91 18:42	0.1708333	10	15	40	16806	185803	544	202609	1.015	9.785	0.043	-0.56054	
3/30/91 19:18	0.1958333	10	15	40	16572	192019	481	208591	1.001	10.112	0.038	-0.868786	
3/30/91 20:21	0.2395833	10	15	40	16466	180280	483	196746	0.994	9.494	0.038	-0.244326	
3/31/91 13:50	0.9680556	10	15	40	64924	178137	371	243061	3.921	9.381	0.029	-3.04914	
3/31/91 14:28	0.9944444	10	15	40	16309	182109	333	198418	0.985	9.590	0.026	-0.319314	
3/31/91 14:55	1.0131944	10	15	40	16977	177737	374	194714	1.025	9.360	0.030	-0.132651	
3/31/91 15:45	1.0479167	10	15	40	16671	179109	350	195780	1.007	9.433	0.028	-0.184529	
3/31/91 16:37	1.0840278	10	15	40	18011	178192	330	196203	1.088	9.384	0.026	-0.215583	
3/31/91 17:17	1.1118056	10	16	37.5	16114	180711	2124	196825	0.912	8.922	0.157	-0.35196	
3/31/91 17:58	1.1402778	10	16	37.5	15486	181596	596	197082	0.877	8.966	0.044	-0.246913	
3/31/91 18:32	1.1638889	10	16	37.5	17591	197207	387	214798	0.996	9.737	0.029	-1.12136	
3/31/91 18:51	1.1770833	10	16	37.5	16684	181306	407	197990	0.945	8.951	0.030	-0.286424	
3/31/91 19:28	1.2027778	10	16	37.5	16537	181533	399	198070	0.936	8.963	0.030	-0.288716	
3/31/91 20:26	1.2430556	10	16	37.5	16750	180682	438	197432	0.948	8.921	0.032	-0.261649	
4/1/91 13:30	1.9541667	10	15	40	19842	174765	584	194607	1.198	9.204	0.046	-0.165753	
4/1/91 14:00	1.975	10	15	40	22413	174583	524	196996	1.354	9.194	0.041	-0.306698	
4/1/91 14:30	1.9958333	10	15	40	22030	187971	547	210001	1.330	9.899	0.043	-0.990444	
4/1/91 15:37	2.0423611	10	15	40	23418	174756	516	198174	1.414	9.203	0.041	-0.375872	
4/1/91 16:42	2.0875	10	14	42.8571	24032	172920	504	196952	1.555	9.757	0.043	-0.337837	
4/1/91 17:56	2.1388889	10	14	42.8571	23356	176150	478	199506	1.511	9.939	0.040	-0.474148	
4/1/91 18:36	2.1666667	10	14	42.8571	29881	175354	468	205235	1.934	9.894	0.040	-0.850598	
4/1/91 19:11	2.1909722	10	14	42.8571	23630	181548	5848	205178	1.529	10.244	0.495	-1.251061	
4/1/91 20:21	2.2395833	10	14	42.8571	22129	174334	562	196463	1.432	9.837	0.048	-0.299395	
4/2/91 10:54	2.8458333	10	14	42.8571	30111	162237	396	192348	1.948	9.154	0.034	-0.119256	
4/2/91 12:59	2.9326389	10	14	42.8571	30035	167166	512	197201	1.943	9.432	0.043	-0.402278	
4/2/91 15:08	3.0222222	10	14	42.8571	31174	168784	563	199958	2.017	9.524	0.048	-0.571593	
4/2/91 15:58	3.0569444	10	14	42.8571	30516	162159	543	192675	1.975	9.150	0.046	-0.153506	
4/3/91 11:40	3.8777778	30	43	41.8605	30520	160316	494	190836	1.929	8.835	0.041	-0.044564	
4/3/91 13:25	3.9506944	30	43	41.8605	30485	161647	522	192132	1.927	8.909	0.043	-0.118022	
4/3/91 13:35	3.9576389	30	43	41.8605	30679	163123	528	193802	1.939	8.990	0.044	-0.212126	
4/3/91 15:55	4.0548611	30	43	41.8605	32413	164020	480	196433	2.049	9.040	0.040	-0.367186	
4/3/91 19:12	4.1916667	30	43	41.8605	33467	162610	504	196077	2.115	8.962	0.042	-0.358076	
4/4/91 10:50	4.8430556	30	43	41.8605	31703	155539	461	187242	2.004	8.572	0.038	0.146672	
4/4/91 12:02	4.8930556	30	43	41.8605	32328	155966	450	188294	2.043	8.596	0.037	0.084547	
4/4/91 14:00	4.975	30	43	41.8605	33384	159804	484	193188	2.110	8.807	0.040	-0.196529	
4/4/91 14:57	5.0145833	30	43	41.8605	34200	161250	447	195450	2.162	8.887	0.037	-0.324736	
4/4/91 15:49	5.0506944	30	43	41.8605	33920	160542	494	194462	2.144	8.848	0.041	-0.271906	
4/4/91 18:02	5.1430556	30	43	41.8605	32856	160882	517	193738	2.077	8.867	0.043	-0.225299	
4/5/91 8:54	5.7625	30	44	40.9091	33275	159704	524	192979	2.055	8.602	0.042	-0.183177	
4/5/91 9:50	5.8013889	30	44	40.9091	33622	160286	538	193908	2.077	8.633	0.043	-0.237087	
4/5/91 10:40	5.8361111	30	44	40.9091	33966	160654	508	194620	2.098	8.653	0.041	-0.275731	
4/5/91 11:26	5.8680556	30	44	40.9091	44855	150360	182	195215	2.770	8.098	0.015	-0.367514	500 C
4/5/91 12:09	5.8979167	30	44	40.9091	55596	135923	0	191519	3.434	7.321	0.000	-0.238648	
4/5/91 12:54	5.9291667	30	44	40.9091	55782	137215	50	192997	3.445	7.390	0.004	-0.323764	
4/5/91 13:36	5.9583333	30	44	40.9091	53945	137445	0	191390	3.332	7.403	0.000	-0.218648	

Also used calibration #5 from 4/14 - 4/15.

		rate	flow	Q	Areas				Produced				
actual time	total time	cc	time (s)	cc / min	CO	CO2	CH4	Aco+Aco2	CO	CO2	CH4	carbon	
4/5/91 15:07	6.0215278	30	44	40.9091	53732	137585	0	191317	3.319	7.410	0.000	-0.213033	
4/5/91 18:43	6.1715278	30	44	40.9091	54868	139511	0	194379	3.389	7.514	0.000	-0.386933	
4/6/91 10:55	6.8465278	30	44	40.9091	49804	135332	64	185136	3.076	7.289	0.005	0.145758	
4/6/91 11:40	6.8777778	30	44	40.9091	50892	136575	0	187467	3.143	7.356	0.000	0.01678	
4/6/91 12:24	6.9083333	30	44	40.9091	51400	138479	0	189879	3.175	7.459	0.000	-0.117147	
4/6/91 13:10	6.9402778	30	44	40.9091	54749	137439	55	192188	3.382	7.403	0.004	-0.272429	
4/6/91 14:40	7.0027778	30	44	40.9091	53273	143190	0	196463	3.290	7.712	0.000	-0.48657	
4/6/91 15:55	7.0548611	30	45	40	52114	135250	0	187364	3.147	7.123	0.000	0.012387	
4/6/91 16:49	7.0923611	30	45	40	50869	135813	0	186682	3.072	7.152	0.000	0.057926	
4/6/91 21:03	7.26875	30	45	40	50379	139030	0	189409	3.043	7.322	0.000	-0.0819	
4/6/91 21:46	7.2986111	30	45	40	49946	138194	0	188140	3.016	7.278	0.000	-0.011723	
4/6/91 22:34	7.3319444	30	45	40	49151	138330	0	187481	2.968	7.285	0.000	0.029127	
4/6/91 23:19	7.3631944	30	45	40	50339	135446	0	185785	3.040	7.133	0.000	0.109262	
4/7/91 0:05	7.3951389	30	45	40	50259	133411	69	183670	3.035	7.026	0.005	0.215812	
4/7/91 11:19	7.8631944	30	45	40	49422	136386	52	185808	2.985	7.183	0.004	0.11103	
4/7/91 12:02	7.8930556	30	45	40	49172	136922	64	186094	2.970	7.211	0.005	0.096952	
4/7/91 12:56	7.9305556	30	45	40	30535	160271	666	190806	1.844	8.440	0.053	-0.054709	400 C
4/7/91 13:41	7.9618056	30	45	40	29788	161980	669	191768	1.799	8.530	0.053	-0.099835	
4/7/91 14:37	8.0006944	30	45	40	29406	163710	652	193116	1.776	8.622	0.052	-0.166529	
4/7/91 15:18	8.0291667	30	45	40	31265	161837	484	193102	1.888	8.523	0.038	-0.166887	
4/7/91 16:04	8.0611111	30	45	40	27785	165451	669	193236	1.678	8.713	0.053	-0.161663	
4/7/91 16:45	8.0895833	30	45	40	28052	163505	639	191557	1.694	8.611	0.050	-0.072934	
4/7/91 17:30	8.1208333	30	45	40	27411	162069	615	189480	1.655	8.535	0.049	0.043299	
4/7/91 21:00	8.2666667	30	45	40	28625	163907	467	192532	1.729	8.632	0.037	-0.11512	
4/7/91 21:47	8.2993056	30	45	40	28596	162280	514	190876	1.727	8.546	0.041	-0.031399	
4/7/91 22:37	8.3340278	30	45	40	26701	161969	580	188670	1.613	8.530	0.046	0.09421	
4/7/91 23:23	8.3659722	30	45	40	26846	161862	450	188708	1.621	8.524	0.036	0.101359	
4/8/91 0:25	8.4090278	30	45	40	27974	162510	463	190484	1.689	8.558	0.037	-0.001917	
4/8/91 10:35	8.8326389	30	44	40.9091	24925	161044	418	185969	1.540	8.674	0.034	0.268958	
4/8/91 11:15	8.8604167	30	44	40.9091	27515	158741	342	186256	1.699	8.550	0.028	0.239167	
4/8/91 11:58	8.8902778	30	44	40.9091	26064	160207	384	186271	1.610	8.629	0.031	0.246436	
4/8/91 12:40	8.9194444	30	44	40.9091	27434	160638	385	188072	1.694	8.652	0.031	0.138522	
4/8/91 13:32	8.9555556	30	44	40.9091	27010	162336	342	189346	1.668	8.743	0.028	0.076731	
4/8/91 14:15	8.9854167	30	44	40.9091	27145	160804	349	187949	1.677	8.661	0.028	0.150341	
4/8/91 15:14	9.0263889	30	44	40.9091	27541	163636	340	191177	1.701	8.814	0.027	-0.025924	
4/8/91 16:22	9.0736111	30	44	40.9091	27665	163747	365	191412	1.709	8.819	0.029	-0.041581	
4/8/91 17:11	9.1076389	30	40	45	26691	165334	332	192025	1.813	9.795	0.030	-0.070655	
4/8/91 19:37	9.2090278	30	40	45	25586	167047	346	192633	1.738	9.897	0.031	-0.098312	
4/8/91 22:09	9.3145833	30	40	45	22882	165568	441	188450	1.555	9.809	0.039	0.164584	
4/8/91 22:50	9.3430556	30	43	41.8605	23902	160001	372	183903	1.511	8.818	0.031	0.401155	
4/9/91 10:37	9.8340278	30	42	42.8571	25065	157313	368	182378	1.622	8.876	0.031	0.487462	
4/9/91 11:37	9.8756944	30	42	42.8571	25782	158028	326	183810	1.668	8.917	0.028	0.404279	
4/9/91 12:31	9.9131944	30	42	42.8571	25102	159013	333	184115	1.624	8.972	0.028	0.392108	
4/9/91 13:13	9.9423611	30	42	42.8571	28389	157667	321	186056	1.837	8.896	0.027	0.256381	
4/9/91 13:59	9.9743056	30	43	41.8605	27095	160958	344	188053	1.712	8.871	0.028	0.148923	
4/9/91 14:50	10.009722	30	42	42.8571	39455	146968	113	186423	2.553	8.293	0.010	0.161637	500 C
4/9/91 15:32	10.038889	30	43	41.8605	50527	134788	0	185315	3.193	7.429	0.000	0.138726	
4/9/91 16:41	10.086806	30	43	41.8605	46431	137357	0	183788	2.935	7.570	0.000	0.256016	
4/9/91 17:27	10.11875	30	43	41.8605	46725	135572	0	182297	2.953	7.472	0.000	0.335811	
4/10/91 10:16	10.819444	30	42	42.8571	44987	130853	0	175840	2.911	7.383	0.000	0.722538	500
4/10/91 11:16	10.861111	30	42	42.8571	45165	132302	0	177467	2.922	7.465	0.000	0.62926	502
4/10/91 11:39	10.877083	30	42	42.8571	46321	131444	0	177765	2.997	7.417	0.000	0.602872	498
4/10/91 12:22	10.906944	30	42	42.8571	45793	132565	0	178358	2.963	7.480	0.000	0.573784	499
4/10/91 13:01	10.934028	30	42	42.8571	46324	133276	0	179600	2.997	7.520	0.000	0.499307	498
4/10/91 13:58	10.973611	30	42	42.8571	89803	102749	0	192552	5.811	5.798	0.000	-0.591586	602
4/10/91 14:20	10.988889	30	42	42.8571	68327	112033	0	180360	4.421	6.321	0.000	0.274204	597

		rate	flow	Q	Areas				Produced				
actual time	total time	cc	time (s)	cc / min	CO	CO2	CH4	Aco+Aco2	CO	CO2	CH4	carbon	
4/10/91 15:22	11.031944	30	43	41.8605	68365	112489	0	180854	4.321	6.200	0.000	0.240294	598
4/10/91 15:59	11.057639	30	43	41.8605	68184	115041	0	183225	4.309	6.340	0.000	0.111086	600
4/10/91 16:49	11.092361	30	44	40.9091	68839	112638	0	181477	4.252	6.067	0.000	0.197531	599
4/10/91 20:31	11.246528	30	44	40.9091	64688	118950	0	183638	3.995	6.407	0.000	0.113953	598
4/10/91 22:06	11.3125	30	44	40.9091	62015	118092	0	180107	3.830	6.360	0.000	0.325264	597
4/10/91 22:52	11.344444	30	44	40.9091	60992	117864	0	178856	3.767	6.348	0.000	0.400731	598
4/10/91 23:55	11.388194	30	43	41.8605	61077	117221	0	178298	3.860	6.460	0.000	0.440116	598
4/11/91 0:45	11.422917	30	43	41.8605	47612	95767	0	143379	3.009	5.278	0.000	2.473523	596
4/11/91 1:19	11.446528	30	43	41.8605	58892	114704	0	173596	3.722	6.322	0.000	0.716931	593
4/11/91 6:49	11.675694	30	43	41.8605	61905	119195	0	181100	3.913	6.569	0.000	0.278991	604
4/11/91 7:27	11.702083	30	43	41.8605	61713	119923	0	181636	3.900	6.609	0.000	0.251004	600
4/11/91 8:07	11.729861	30	43	41.8605	61232	119818	0	181050	3.870	6.604	0.000	0.287191	604
4/11/91 9:43	11.796528	30	43	41.8605	58673	121614	0	180287	3.708	6.703	0.000	0.349942	602
4/11/91 10:34	11.831944	30	42	42.8571	58385	124121	0	182506	3.778	7.004	0.000	0.235451	603
4/11/91 15:00	12.016667	30	43	41.8605	59906	127694	0	187600	3.786	7.038	0.000	-0.063073	605
4/11/91 21:35	12.290972	30	44	40.9091	57526	128575	0	186101	3.553	6.925	0.000	0.037911	597
4/11/91 23:30	12.370833	30	42	42.8571	11767	177562	346	189329	0.761	10.019	0.029	0.207241	403
4/12/91 0:14	12.401389	30	42	42.8571	12667	175697	383	188364	0.820	9.914	0.032	0.251105	399
4/12/91 17:25	13.117361	30	42	42.8571	13664	176747	274	190411	0.884	9.973	0.023	0.136574	400
4/12/91 22:22	13.323611	30	42	42.8571	13263	169749	328	183012	0.858	9.578	0.028	0.552813	406
4/12/91 23:13	13.359028	30	41	43.9024	13622	171347	352	184969	0.903	9.904	0.031	0.448052	403
4/13/91 22:23	14.324306	30	42	42.8571	13167	173899	322	187066	0.852	9.812	0.027	0.325369	
4/13/91 23:09	14.35625	30	41	43.9024	13561	172762	312	186323	0.899	9.986	0.027	0.373776	402

Progress Report (Subcontract SK90A027) June, 1991

A single reactor run has been made during this period which started on June 4, 1991 and has continued as of mid-July. The reaction study has involved Fe/SiO_2 catalyst at 500°C. Our previous reaction studies with Fe/SiO_2 have been either at 400°C or at 600°C. At 600°C, we observe catalyst deactivation with time. However, at 400°C, slight deactivation is observed during the first one or two days of operation, after which the catalytic activity increases surpassing even the initial activity and eventually attaining a much higher activity after approximately a 200 hr period. We have attributed this increased activity to a faceting or breaking up of the iron (or iron carbide) particles which increases the surface area and hence the activity. The increased surface area is also evidenced by an increase in surface roughness as observed by SEM (scanning electron microscopy).

We began this run at 500°C with a view to examine the transient behavior at temperature intermediate between the two extremes (400°C and 600°C).

The catalyst was subjected to in situ pretreatment before starting the reaction. It was initially subjected to oxidation by O_2/He gas mixture for one hour at 100°C and for four hours at 400°C. Following this the reactor was flushed with helium for half an hour. Subsequently the catalyst was reduced in a hydrogen atmosphere overnight at 400°C. The heating up of the reactor to 500°C before starting the reaction was done when hydrogen was flowing. The reaction was started at 500°C with a gas mixture containing 10% CO_2, 20% H_2 and 70% He.

Figure 1 shows the transient activity behavior for the first fifteen days of operation. The transient behavior is remarkably similar to that observed previously at 400°C; the catalyst deactivates during the initial 20 hours of operation, but then the activity increases four-fold over next 200 hours of operation. After 15 days of reactor operation when the catalyst had attained pseudo-steady state, we began conducting kinetic experiments, with the following objectives:

1. To study the rate of reaction keeping the partial pressure of hydrogen constant and varying that of the carbon dioxide.

2. To find the rate of reaction keeping the partial pressure of the carbon dioxide constant while varying that of the hydrogen.

3. To get the rate of the reaction at various degrees of dilution of the reactant (i.e. keeping the ratio of hydrogen to the carbon dioxide constant) with He.

At the end of June 30, 1991, we have almost finished the runs with the first objective in mind. For each data point, we have insured the steady state catalytic behavior by monitoring reactor operation over a period of one to two days. The rates of formation of CO and CH_4 and rate of consumption of CO_2 were found to be constant over this period of time. The various rates obtained are summarized in Table I.

It is seen from the results that when the reactant stream was diluted by 50% the rates approximately halved suggesting that the power of the partial pressure

term of H_2 and CO_2 in the rate expression. When 10% of methane was added to the reactant stream it didn't alter the rates significantly implying that the effect of methane on the hydrogenation of CO_2 over iron catalyst is negligible.

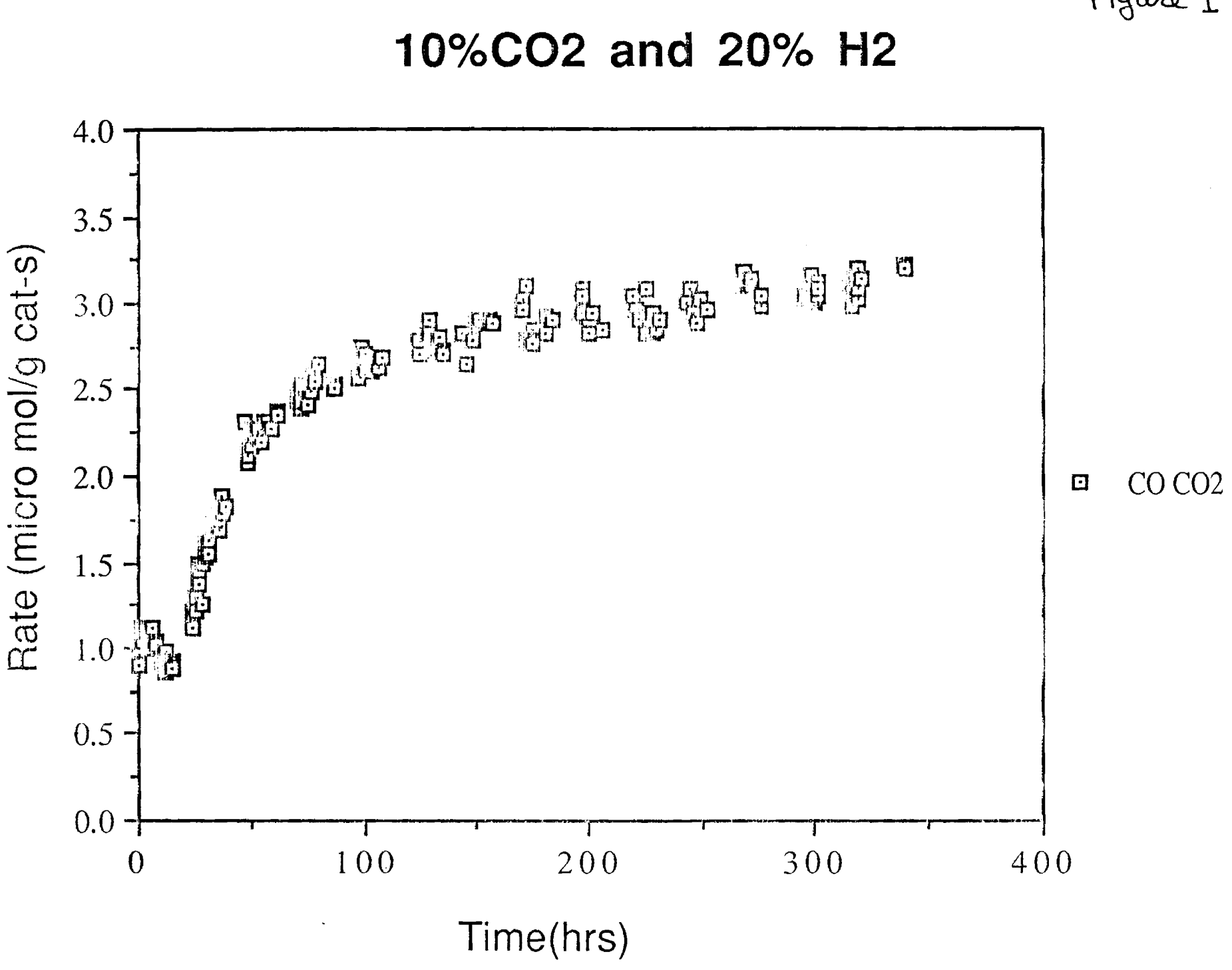
The rates observed for the case in which we vary the partial pressure of CO_2 suggests a square root dependence but this results can be confirmed only after finishing all the experiment. It is also not known whether in the rate expression the partial pressure term of the reactant species will be independent or will it be of the form shown below:

$$\text{Rate} = k\frac{P_{co_2}^{m} P_{H_2}^{n}}{1 + k_2 P_{H_2}^{q}}$$

Table I

Reactant Mixture	Component	Rate (micro mol/gcat-s)
10% CO_2, 20% H_2	CO_2	3.3
70% He	CO	3.3
5% CO_2, 10% H_2	CO_2	1.55
85% He	CO	1.55
5% CO_2, 10% H_2	CO_2	1.45
10% CH_4, 75% He	CO	1.45
5% CO_2, 20% H_2	CO_2	2.9
75% He	CO	2.7
	CH_4	0.18
2.5% CO_2, 20% H_2	CO_2	1.728
77.5% He	CO	1.45
	CH_4	0.27

Figure 1


10%CO2 and 20% H2
Rate (micro mol/g cat-s)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
Time(hrs)
CO CO2

E-19-627

Georgia Institute of Technology
School of Chemical Engineering
Atlanta, Georgia 30332-0100
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(404) 894- 2826

DESIGNING TOMORROW TODAY

August 11, 1991

Ms. Robin McElyea
McDonnell Douglas Space Systems
Huntsville Division
689 Discovery drive
Huntsville, Alabama 35806

RE : Monthly Progress Report/ Subcontract SK90A027

Dear Ms. McElyea :

Please find enclosed the monthly progress report for July,1991. I may be reached at (404) 894-2826, should you have any questions.

Best regards.

Sincerely,

Pradeep K. Agrawal
Associate Professor

Progress Report (Subcontract SK90A027) July,1991

In last month's progress report, we had provided partial results of our kinetic studies at 500 ^{o}C over Fe/SiO_2 catalyst. During the almost entire month of July,1991, reactor studies were continued with the same catalyst which was started in the first week of june,1991. Our kinetic studies at 500 ^{o}C have been completed. The results are given in the enclosed tables and figures, and will be summarized below briefly. It is important to mention here also that we have initiated the run at 400 ^{o}C to obtain kinetic behavior at lower temperature; we plan to do similar run at 600 ^{o}C also.

The following observations can be made at 500 ^{o}C :

1. The reaction rate is proportional to the square root of the concentration of carbon dioxide.

2. The reaction rate is proportional to the square root of the concentration of hydrogen.

3. The presence of methane has negligible effect on the reaction rate.

4. The reaction rate is linearly proportinal to the total pressure, which is consistent with the first two conclusions.

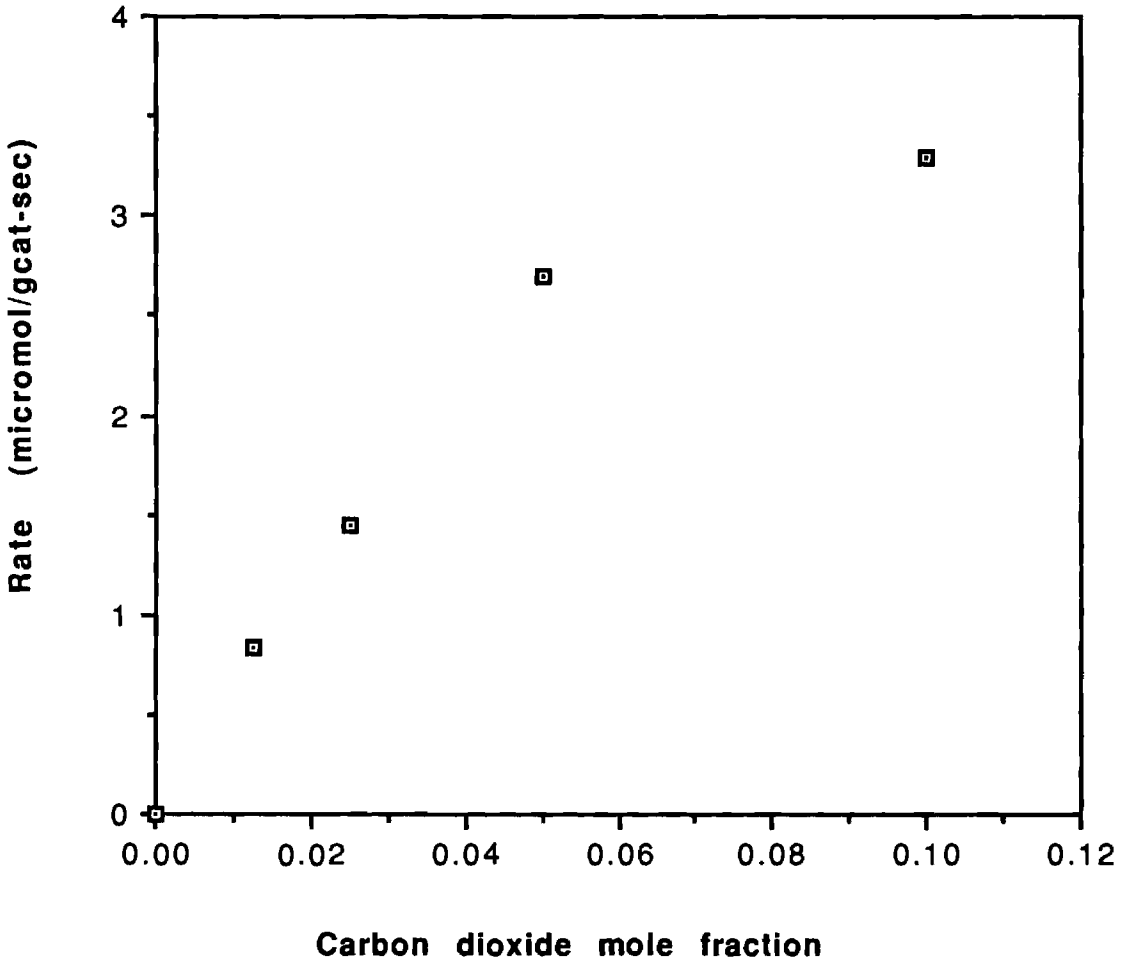
Table 1

Reactant Mixture	Component	Rate(micro mol/gcat-s)
1.25% CO_2 , 20% H_2	CO_2	1.0
78.75% He	CO	0.84
	CH_4	0.15
10% CO_2 , 20% H2	CO_2	3.3
70% He	CO	3.3
10% CO_2 , 16% H2	CO_2	3.5
74% He	CO	3.5
10% CO_2 , 12% H2	CO_2	2.9
78% He	CO	2.9
10% CO_2 , 8% H2	CO_2	2.25
82% He	CO	2.25
10% CO_2 , 4% H2	CO_2	1.55
86% He	CO	1.55
10% CO_2 , 2% H2	CO_2	1.03
88% He	CO	1.03

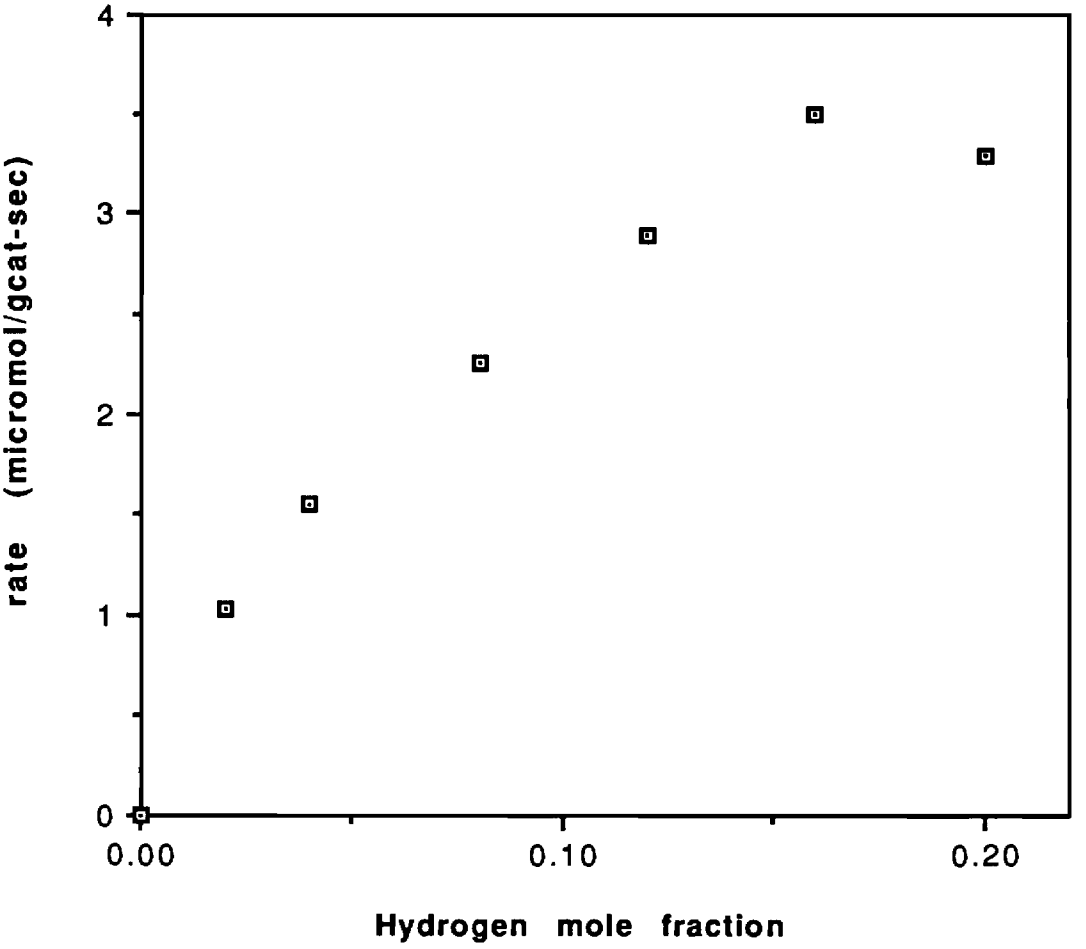
Table I

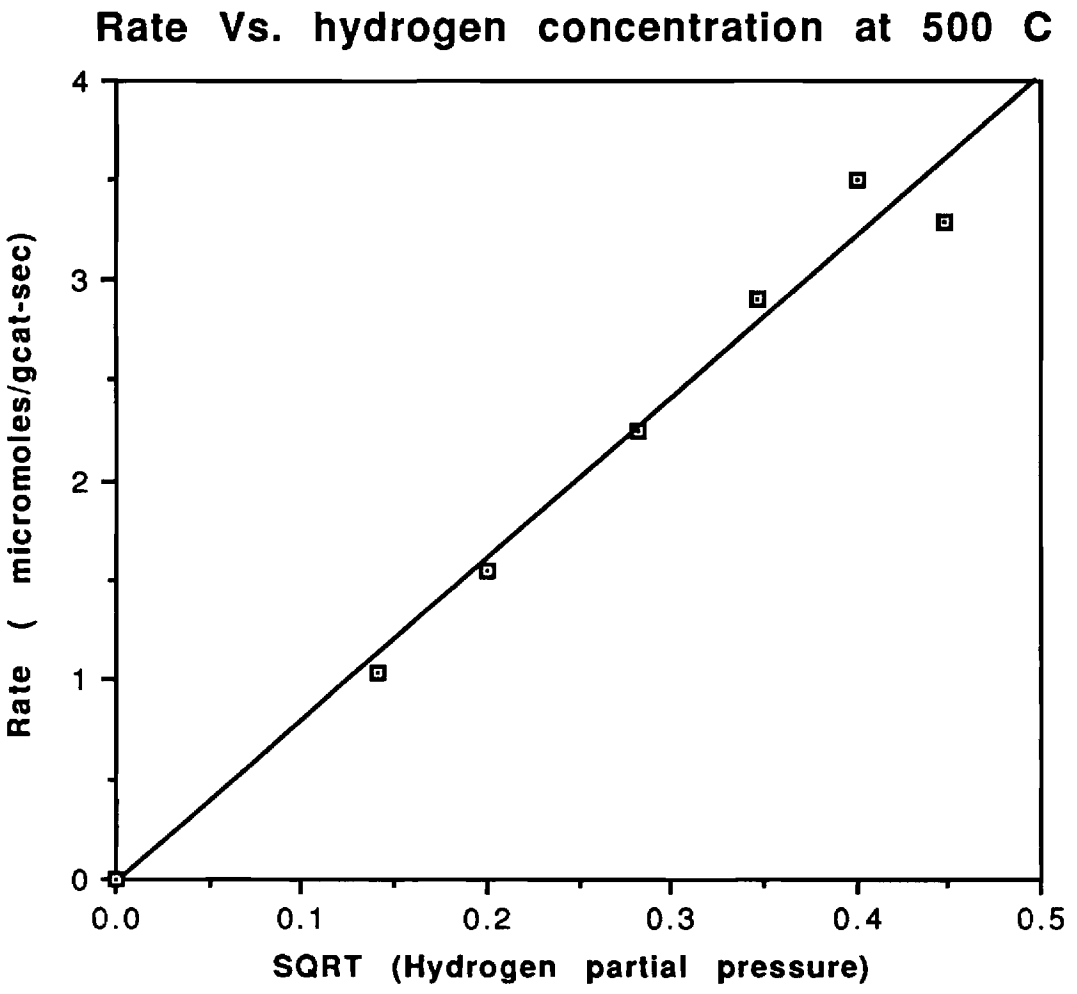
Reactant Mixture	Component	Rate (micro mol/gcat-s)
10% CO_2, 20% H_2	CO_2	3.3
70% He	CO	3.3
5% CO_2, 10% H_2	CO_2	1.55
85% He	CO	1.55
5% CO_2, 10% H_2	CO_2	1.45
10% CH_4, 75% He	CO	1.45
5% CO_2, 20% H_2	CO_2	2.9
75% He	CO	2.7
	CH_4	0.18
2.5% CO_2, 20% H_2	CO_2	1.728
77.5% He	CO	1.45
	CH_4	0.27

Rate Vs. Carbon dioxide concentration

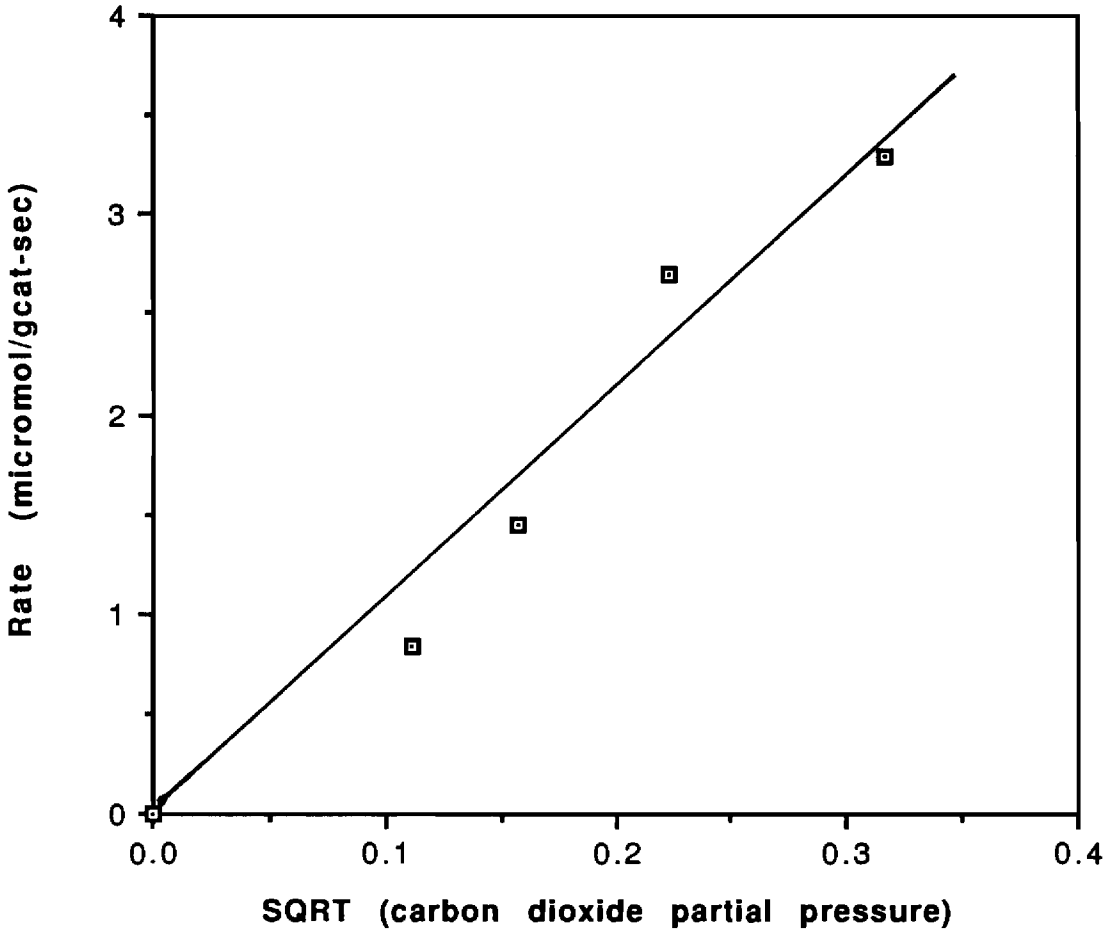


Rate Vs. hydrogen mole fraction at 500 C




Rate Vs. hydrogen concentration at 500 C
Rate (micromoles/gcat-sec)
SQRT (Hydrogen partial pressure)
0
1
2
3
4
0.0
0.1
0.2
0.3
0.4
0.5

Rate Vs. carbon dioxide conc. at 500 C



Georgia Tech

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September 16, 1991

Ms. Robin McElyea
McDonnell Douglas Space Systems
Huntsville Division
689 Discovery Drive
Huntsville, Alabama 35806

RE: **MONTHLY PROGRESS REPORT/SUBCONTRACT SK90A027**

Dear Ms. McElyea:

Please find enclosed the monthly progress report for August 1991. I may be reached at (404) 894-2826 should you have any questions.

Best regards.

Sincerely,

Pradeep K. Agrawal
Associate Professor

/st

PROGRESS REPORT (Subcontract SK90A027)
August 1991

We have completed the kinetic studies of Fe/SiO_2 catalyst at 400 °C during the month of August, 1991 and have begun similar studies at 600°C. The results are given in the enclosed tables and figures, and are briefly summarized below:

1. The reaction rate increases with increasing hydrogen partial pressure.

2. The reaction rate increases with increasing carbon dioxide partial pressure.

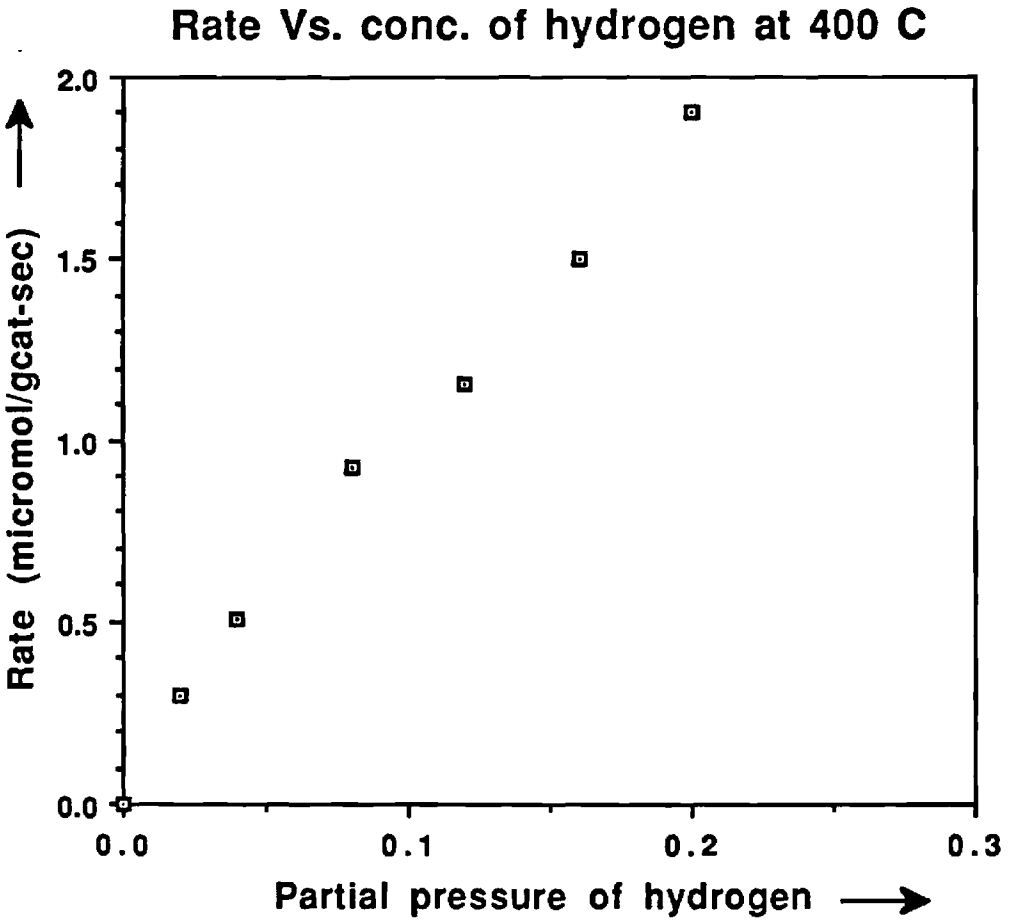
3. The reaction rate is linearly proportional to the total reactor pressure, while maintaining the same feed composition.

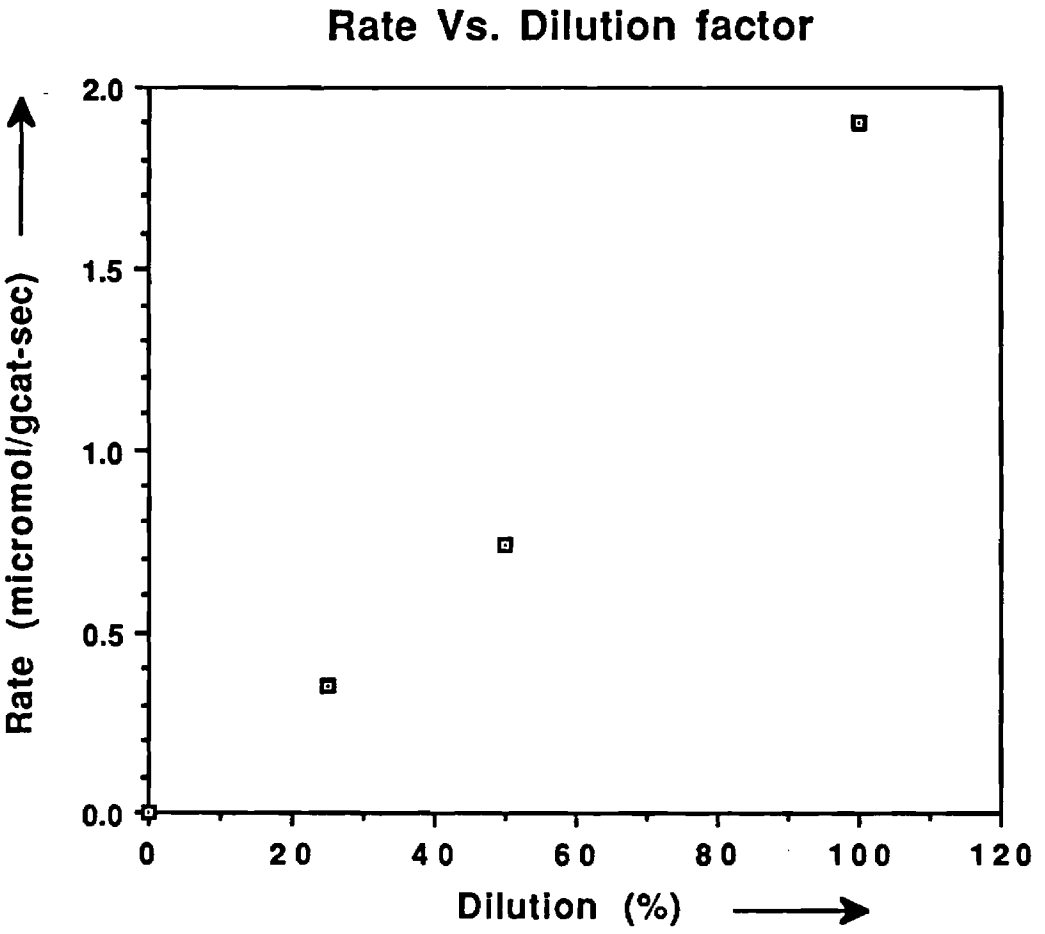
The efforts are underway to fit the observed kinetic behavior (at 400°C & 500°C) with a nonlinear mechanistic model. At the same time, we are trying to complete the kinetic studies at 600°C.

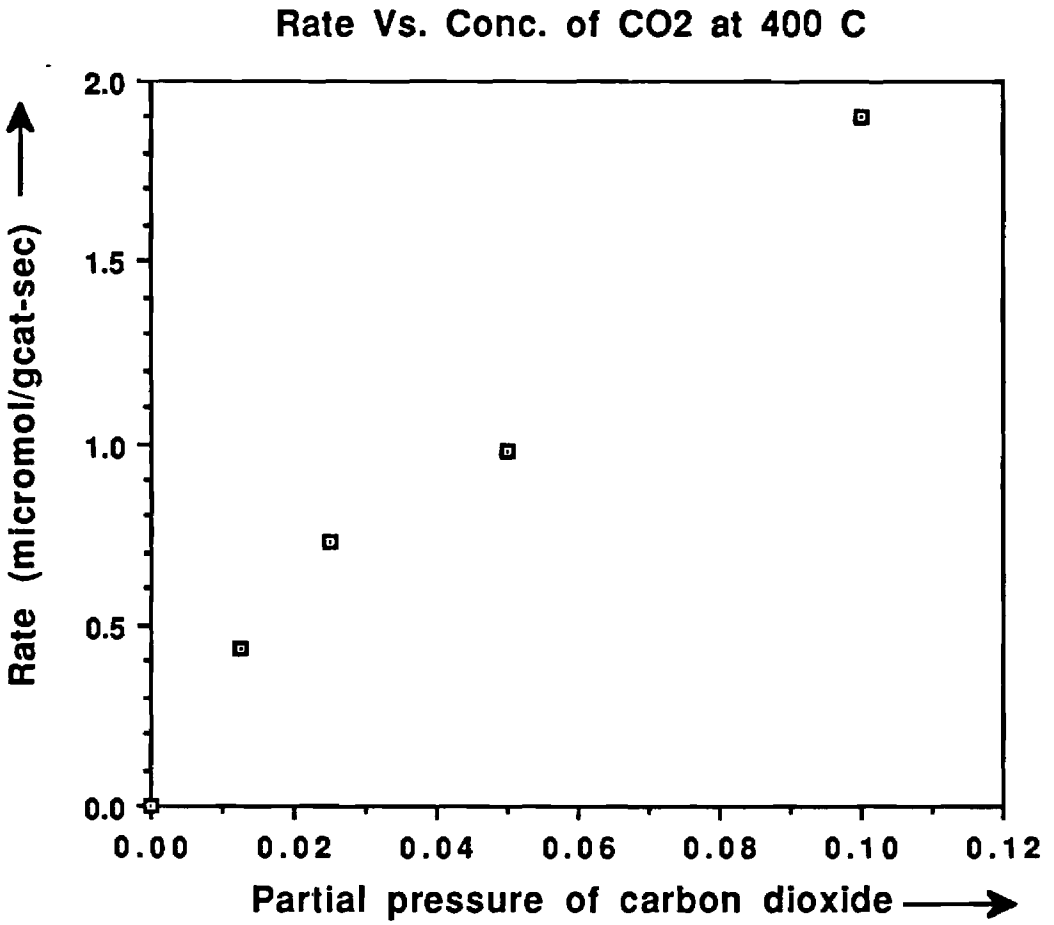
Table 1

TABLE 1

Reactant Mixture	Component	Rate(micro mol/gcat-s)
10% CO_2 , 20% H_2	CO_2	1.9
70% He	CO	1.9
10% CO_2 , 16% H_2	CO_2	1.5
74% He	CO	1.49
	CH_4	0.01
10% CO_2 , 12% H_2	CO_2	1.16
78% He	CO	1.16
10% CO_2 , 8% H_2	CO_2	0.92
82% He	CO	0.92
10% CO_2 , 4% H_2	CO_2	0.51
86% He	CO	0.51
10% CO_2 , 2% H_2	CO_2	0.3
88% He	CO	0.3
5% CO_2 , 10% H_2	CO_2	0.74
85% He	CO	0.74
2.5% CO_2 , 5% H_2	CO_2	0.355
87.5% He	CO	0.355
5% CO_2 , 20% H_2	CO_2	0.98
85% He	CO	0.90
	CH_4	0.04
2.5% CO_2 , 20% H_2	CO_2	0.727
87.5% He	CO	0.65
	CH_4	0.08
1.25% CO_2 , 20% H_2	CO_2	0.435
88.75% He	CO	0.280
	CH_4	0.155


Rate Vs. conc. of hydrogen at 400 C
Rate (micromol/gcat-sec)
2.0
1.5
1.0
0.5
0.0
0.0
0.1
0.2
0.3
Partial pressure of hydrogen


Rate Vs. Dilution factor
Rate (micromol/gcat-sec)
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100
120
Dilution (%)


Rate Vs. Conc. of CO2 at 400 C
Rate (micromol/gcat-sec)
2.0
1.5
1.0
0.5
0.0
0.00
0.02
0.04
0.06
0.08
0.10
0.12
Partial pressure of carbon dioxide

Library does not have Monthly Progress Report for September, 1991

Georgia Tech

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November 15, 1991

Ms. Robin McElyea
McDonnell Douglas Space Systems
Huntsville Division
689 Discovery Drive
Huntsville, AL 35806

RE: Monthly Progress Report/Subcontract SK90A027

Dear Ms. McElyea:

Pleased find enclosed the monthly progress report for October, 1991. I may be reached at (404) 894-2826 should you have any questions.

Best regards.

Sincerely,

Pradeep K. Agrawal
Associate Professor

PROGRESS REPORT (Subcontract sk90a027)

We have completed the kinetic studies of Fe/SiO_2 catalyst at 600 ^oC during the month of October and have begun the studies on the effect of carbon monoxide on the reaction rate at various temperatures. The results are given in the enclosed table and figures and are summarized below:

1. The reaction rate increases with increase in the partial pressure of hydrogen and the relationship seems to be square root relationship between the rate and the partial pressure of hydrogen.

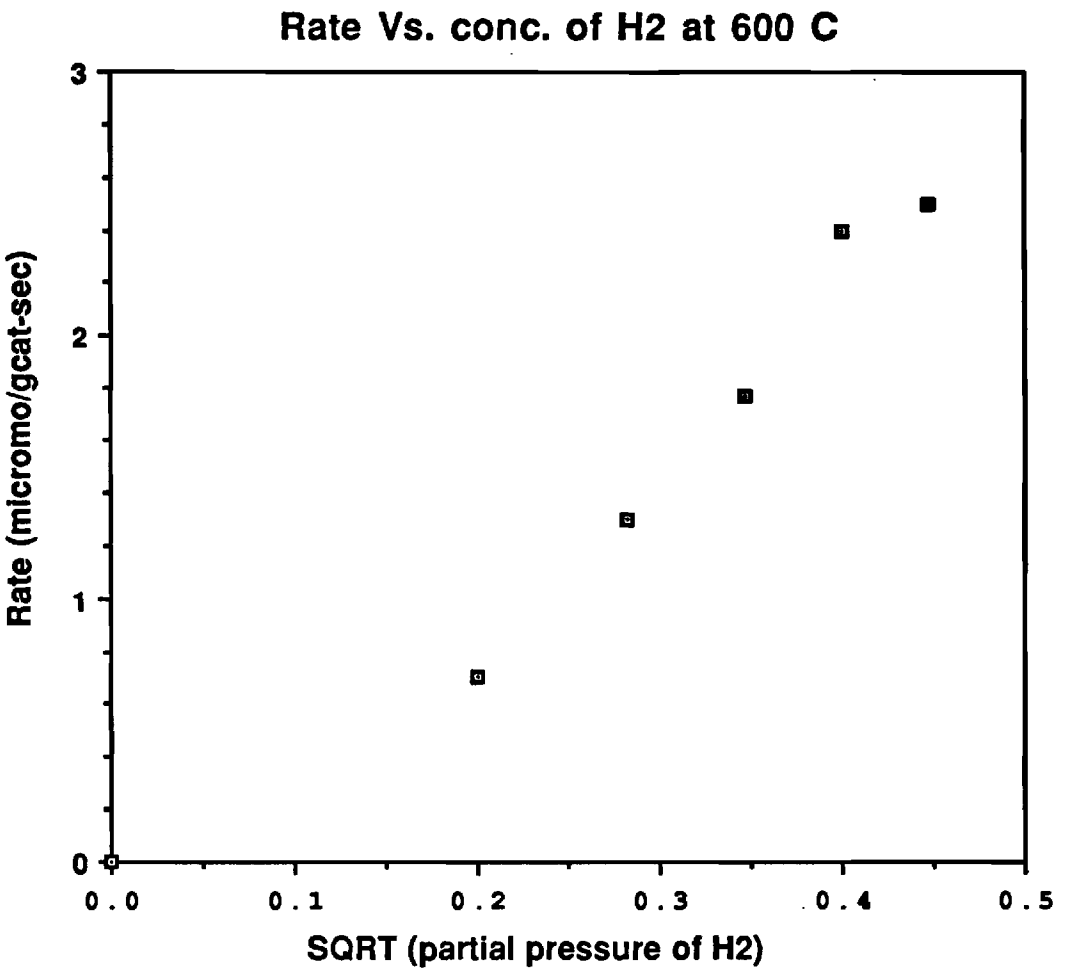
2. the rate also increases with the increase in the concentration of the carbon dioxide . The relationship between the rate and the partial pressure of carbon dioxide is once again square root.

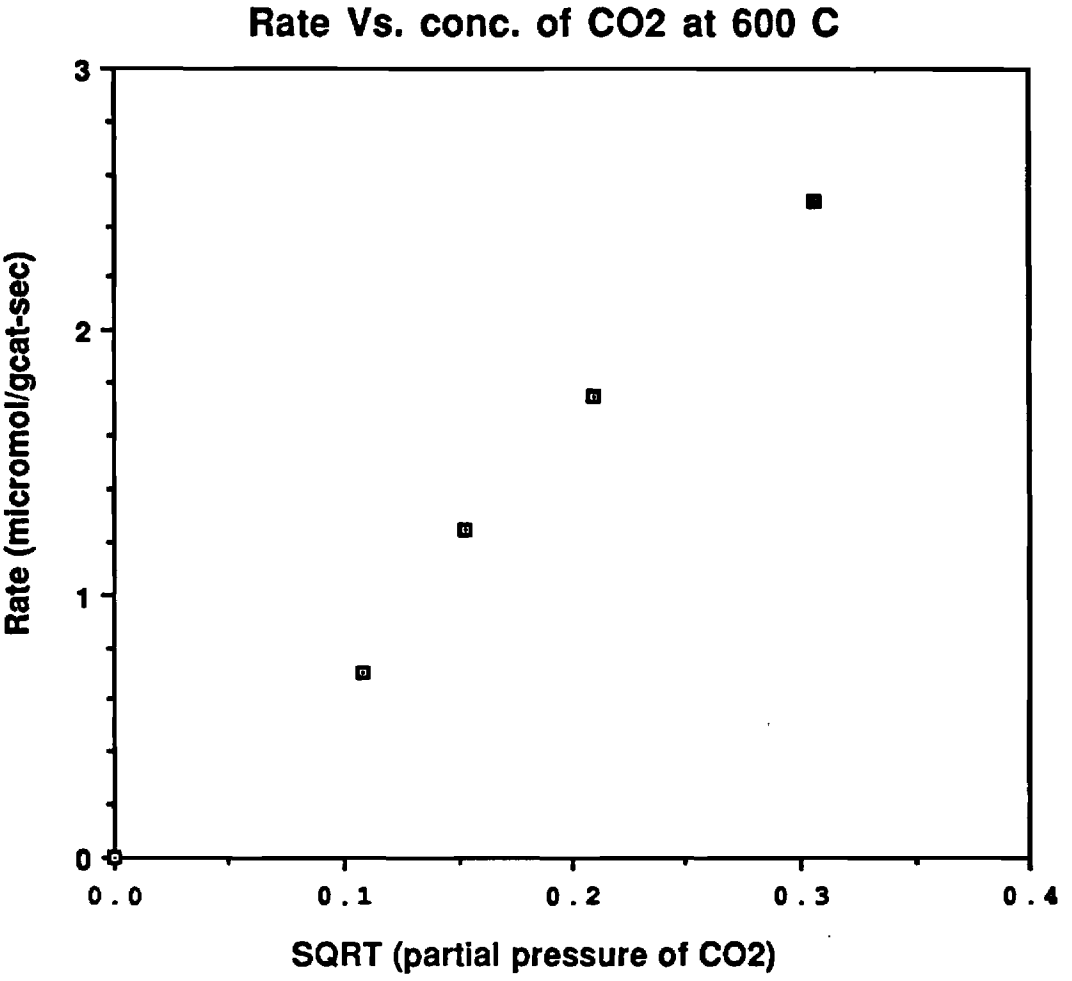
3. The reaction rate is linearly proportional to the total reactor pressure keeping the same feed composition.

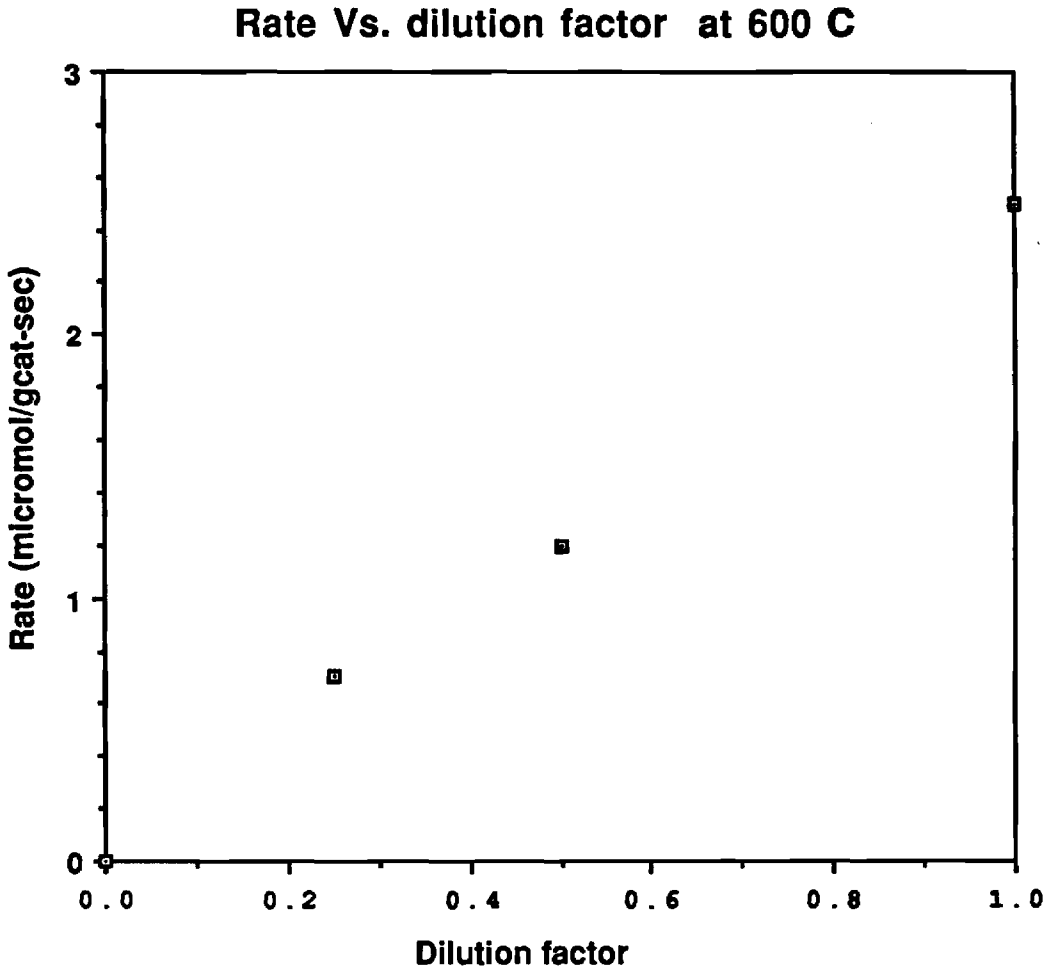
The efforts are underway to model the external transport and also , fit the observed kinetic behaviour with mechanistic model.

Table 1

Reactant mixture	Component	Rate (micromol/gcat-sec)
9.34%CO_2,20% H_2	CO_2	2.5
70.66% He	CO	2.5
9.34%CO_2,16% H_2	CO_2	2.4
74.66% He	CO	2.4
9.34%CO_2,12% H_2	CO_2	1.775
78.66% He	CO	1.775
9.34%CO_2,8% H_2	CO_2	1.3
82.66% He	CO	1.3
9.34%CO_2,4% H_2	CO_2	0.7
86.66% He	CO	0.7
4.67%CO_2,20% H_2	CO_2	1.75
75.33% He	CO	1.75
2.335%CO_2,20% H_2	CO_2	1.25
77.665% He	CO	1.25
1.1675%CO_2,20% H_2	CO_2	0.7
78.8325% He	CO	0.7
4.67%CO_2,10% H_2	CO_2	1.2
85.33% He	CO	1.2
2.335%CO_2,5% H_2	CO_2	2.5
92.665% He	CO	2.5


Rate Vs. conc. of H2 at 600 C
Rate (micromo/gcat-sec)
SQRT (partial pressure of H2)
0
1
2
3
0.0
0.1
0.2
0.3
0.4
0.5


Rate Vs. conc. of CO2 at 600 C
Rate (micromol/gcat-sec)
3
2
1
0
0.0
0.1
0.2
0.3
0.4
SQRT (partial pressure of CO2)


Rate Vs. dilution factor at 600 C
Rate (micromol/gcat-sec)
3
2
1
0
0.0
0.2
0.4
0.6
0.8
1.0
Dilution factor

E-19-659

Georgia Tech

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December 6, 1991

Ms. Robin McElyea
McDonnell Douglas Space Systems
Huntsville Division
689 Discovery Drive
Huntsville, AL 35806

RE: Monthly Progress Report/Subcontract SK90A027

Dear Ms. McElyea:

Please find enclosed the monthly progress report for November 1991. I may be reached at (404) 894-2826 should you have any questions.

Best regards.

Sincerely,

Pradeep K. Agrawal
Associate Professor

PKA/ske

Enclosure

Monthly report :

This month the thrust of the experiments were, to find the effect of carbon monoxide on the rate of the reaction. The effects were studied at two temperatures namely 400 C and 600 C. The three concentration of carbon monoxide used were 1,2 and 4% in the reactant stream. The results so obtained have been summarized in table1-2.

The results show that carbon monoxide reduces the rate of the reaction. The deactivation due to the presence of carbon monoxide appears to be permanent . The deactivation due to the carbon monoxide is more pronounced at 600 C. This can be seen from the fact that the rate of the reaction for 10%CO2 and 20%H2 before and after the kinetic studies is vastly different.

This observation can be explained by the acceleration of Bouduard Reaction namely:

$$2CO = C + CO_2$$

this reaction increases the deposition of the carbon which in turn might be responsible for the permanent deactivation of the catalyst.

Future work will concentrate on the causes for the sudden deactivation at higher temperatures. Our hypothesis for the deactivation should be supplemented by experimental results. This can be done by treating the deactivated catalyst with oxygen and then reducing it with hydrogen at 600 C. Such a process will oxidize any carbon present in the catalyst. If the catalyst regains its initial activity then our hypothesis for the catalyst deactivation would be correct.

Table 1:

Kinetic data obtained at 400 C

Reactant mixture	**Component**	**Rate (micromol/gcat-sec)**
10%CO2 ,20%H2	CO	1.5
70%He	CO2	1.5
(before kinetic studies)		
1%CO,9.5%CO2 ,20%H2	CO	0.95
69%He	CO2	0.95
2%CO,9%CO2 ,20%H2	CO	0.7
69%He	CO2	0.7
4%CO,8%CO2 ,20%H2	CO	0.55
69%He	CO2	0.55
10%CO2 ,20%H2	CO	1.2
70%He	CO2	1.2
(after kinetic studies)		

Table 2:

Kinetic data obtained at 600 C

Reactant mixture	**Component**	**Rate (micromol/gcat-sec)**
10%CO2 ,20%H2	CO	1.5
70%He	CO2	1.5
(before kinetic studies)		
1%CO,9.5%CO2 ,20%H2	CO	0.6
69%He	CO2	0.6
2%CO,9%CO2 ,20%H2	CO	0.4
69%He	CO2	0.4
4%CO,8%CO2 ,20%H2	CO	0.45
69%He	CO2	0.45
10%CO2 ,20%H2	CO	0.6
70%He	CO2	0.6
(after kinetic studies)		

F-19-631

Georgia Tech

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January 17,1992

Ms. Robin McElyea
McDonnell Douglas Space Systems
Huntsville Division
689 Discovery Drive
Huntsville, Al 35806

RE : Monthly Progress Report/ Subcontract SK90A027

Dear Ms. McElyea :

Please find enclosed the monthly progress report for December,1991. Please call me at (404) 894-2826 if you have any questions.

Best wishes for the new year.

Sincerely,

Pradeep K. Agrawal
Associate Professor

The purpose of the experiments done this month were to find the effect of CO in the reactants on the rate of reaction at 600 C and also experimentally find whether internal transport effects are significant.

The experiments to find the effect of CO was done first. The concentration of CO used for the experiments were 1% , 2% and 4% by volume. The results obtained in those experiments are summarized below:

% of CO in reactant stream	**Rate(micromol/gcat-sec)**
No CO present in the stream	1.3
2%	1.2
4%	1.35
1%	1.4

From the results above it is seen that there is no difference between the rate of reaction for different conditions,within the experimental error. This can be explained by the decrease in adsorption of CO with increase in temperature.

The second experiment done was to find about the internal transport effects in the the catalytic reactor. This experiment was accomplished by crushing catalyst to about 1/10 of its size. As it is known that, if the reaction rate remains same even after decrease in the size of the catalyst,then the reactor isn't operating in region where internal transport is significant. After conducting the experiment with crushed catalyst the steady state reaction rate obtained was 1.9 micromol/gcat-s(figure1). This result is comparable to that obtained with pellet which was 1.6 micormol/gcat-s(figure2). This observation is further strengthened by calculation of effectiveness factor from the rates obtained with two different size of the catalyst(appendix1). The calculation sheet is at the end.

Figure 1

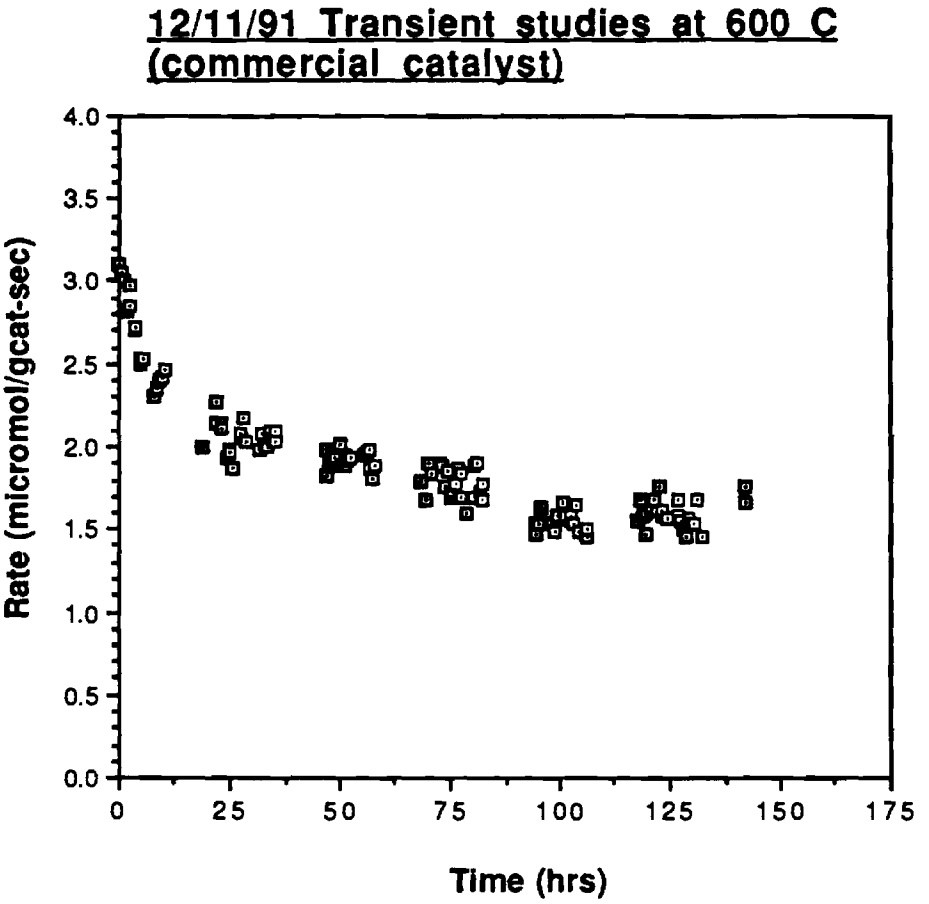
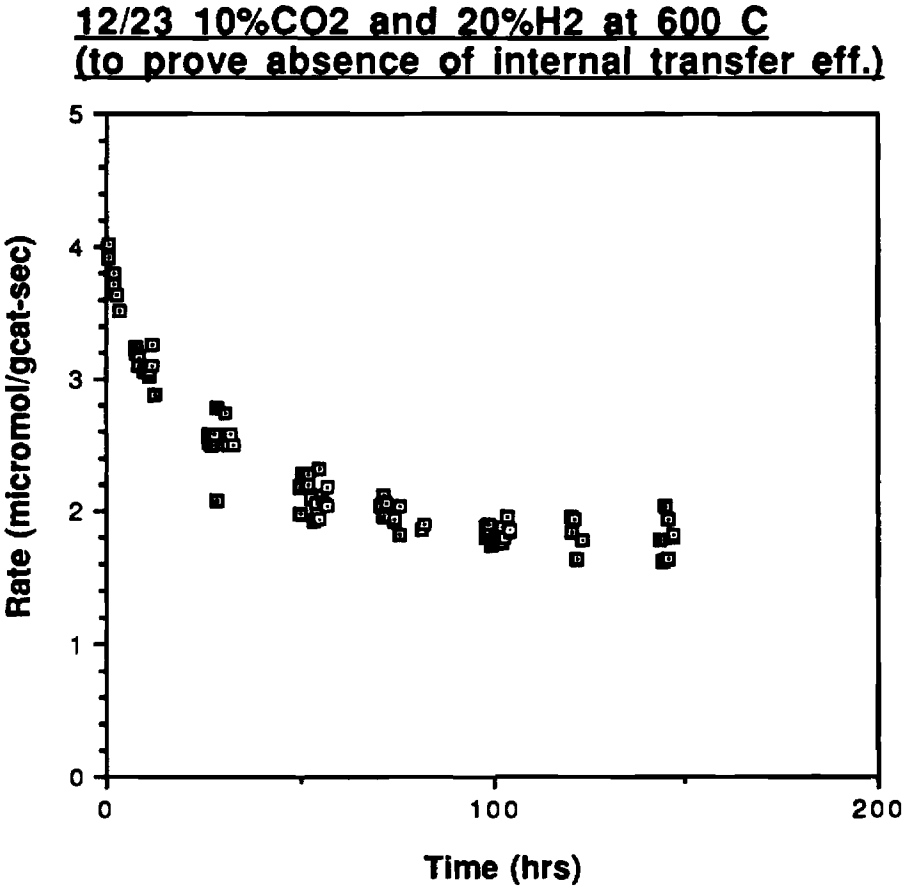

12/11/91 Transient studies at 600 C
(commercial catalyst)
Rate (micromol/gcat-sec)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
25
50
75
100
125
150
175
Time (hrs)

Figure 2


12/23 10%CO2 and 20%H2 at 600 C
(to prove absence of internal transfer eff.)
Rate (micromol/gcat-sec)
0
1
2
3
4
5
0
100
200
Time (hrs)

Appendix 1

Calculation Of Effectiveness Factor

Condition 1: Catalyst pellet

Condition 2: Crushed catalyst

We assume the pellet to be spherical and also the crushed catalyst.

$$\therefore \quad r_1 = \frac{1}{\phi_1}\left(\frac{1}{\tanh 3\phi_1} - \frac{1}{3\phi_1}\right) k_1 c_s \quad -(1)$$

r_1 = Rate of reaction

ϕ_1 = Thiele modulus

k_1 = Reaction rate constant

c_s = Concentration of reactant at surface

As $$\frac{\phi_1}{\phi_2} = \frac{d_1}{d_2} \simeq 10 \quad -(2)$$

$r_1 = 1.6 \ \mu mol/g cat - sec$

$r_2 = 1.9 \ \mu mol/g cat - sec$

The second rate was obtained when amount of CO_2 was 8.52% compared to 9.51% in former case.

As $$r \propto P_{CO_2}^{1/2}$$

$$\therefore \text{ corrected } r_2 = 1.9 * \left(\frac{9.51}{8.52}\right)^{1/2} = 2.0 \ \mu mol/g cat - s$$

$$\frac{r_1}{r_2} = \frac{\phi_2}{\phi_1} \frac{(\coth 3\phi_1 - 1/3\phi_1)}{(\coth 3\phi_2 - 1/3\phi_2)} \quad \text{— (3)}$$

Substituting (2) in (3)

$$\frac{r_1}{r_2} = \frac{1}{10} \left(\frac{\coth 3\phi_1 - 1/3\phi_1}{\coth 0.3\phi_1 - 1/.3\phi_1} \right)$$

$$\Rightarrow \frac{1.6}{2.0} = \frac{1}{10} \left(\frac{\coth 3\phi_1 - 1/3\phi_1}{\coth 0.3\phi_1 - 1/.3\phi_1} \right)$$

$$\Rightarrow 8 = \left(\frac{\coth 3\phi_1 - 1/3\phi_1}{\coth 0.3\phi_1 - 1/0.3\phi_1} \right)$$

By trial & error

$$\phi_1 \leq 0.68 \qquad \eta = 0.9$$

So internal transport effects can be neglected

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February 19, 1992

Ms. Robin McElyea
McDonnell Douglas Space Systems
Huntsville Division
689 Discovery Drive
Huntsville, Al 35806

RE: Monthly Progress Report/ Subcontract SK90A027

Dear Ms. McElyea:

Please find enclosed the monthly progress report for January, 1992. Please call me at (404) 894-2826 if you have any questions.

Best wishes.

Sincerely,

Pradeep K. Agrawal
Associate Professor

The first experiment this month was to confirm the earlier finding that CO didn't affect the reaction at 600 C. As this observation was in direct contrast to the previous study in which it was seen that the catalyst got severely deactivated in presence of CO. From the Table given below it seen that CO doesn't affect the reaction at 600C. This can be explained by the reduction in the tendency of CO monoxide to adsorb at higher temperatures. The previous observation in which it was seen that the catalyst severely deactivated may be due to the fact that there might have been some CO in the reactor while the bypass runs were being done. Consequently the reactor becomes a batch reactor and CO deposits carbon and severely deactivates the catalyst and hence reduction in rate of reaction when the next kinetic experiment is done.

% of CO in reactant stream	**Rate (micromol/gcat-sec)**
No CO present in the stream	1.5
1%	1.6
2%	1.55
4%	1.45

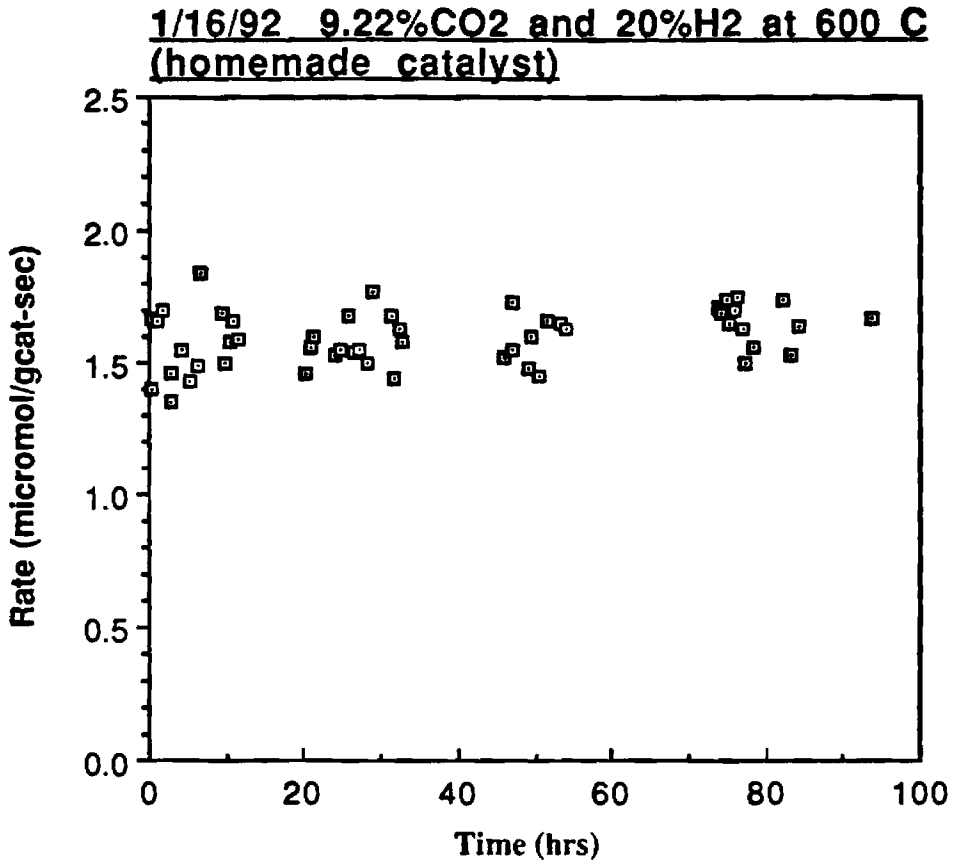
The second part was to find whether the external transport effect was significant as in previous study when external transport effect was studied by changing the flow rate of the reactant stream. The rate increased with increase in the flow rate and decreased with decrease in flow rate which clearly indicated presence of external transport effects. This experiment was done at 600 C at three different flow rates and the data obtained in

summarized below:

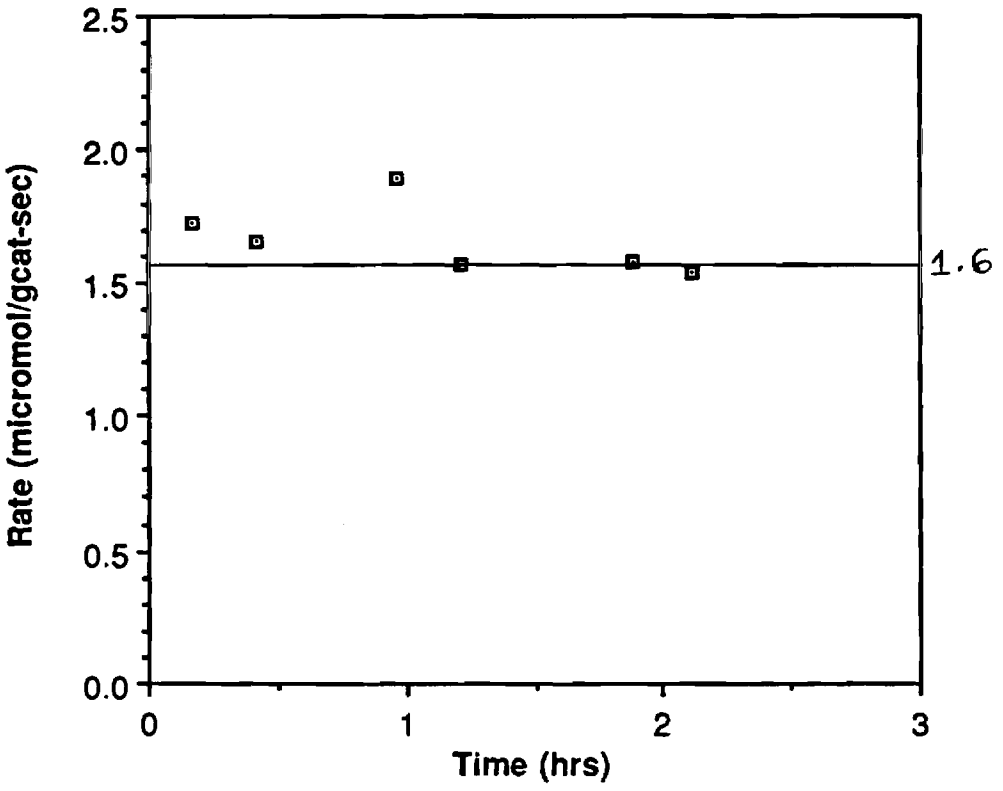
Flow Rate (cc/min)	Rate (micromol/gcat-sec)
20	1.2
40	1.5
80	2.2

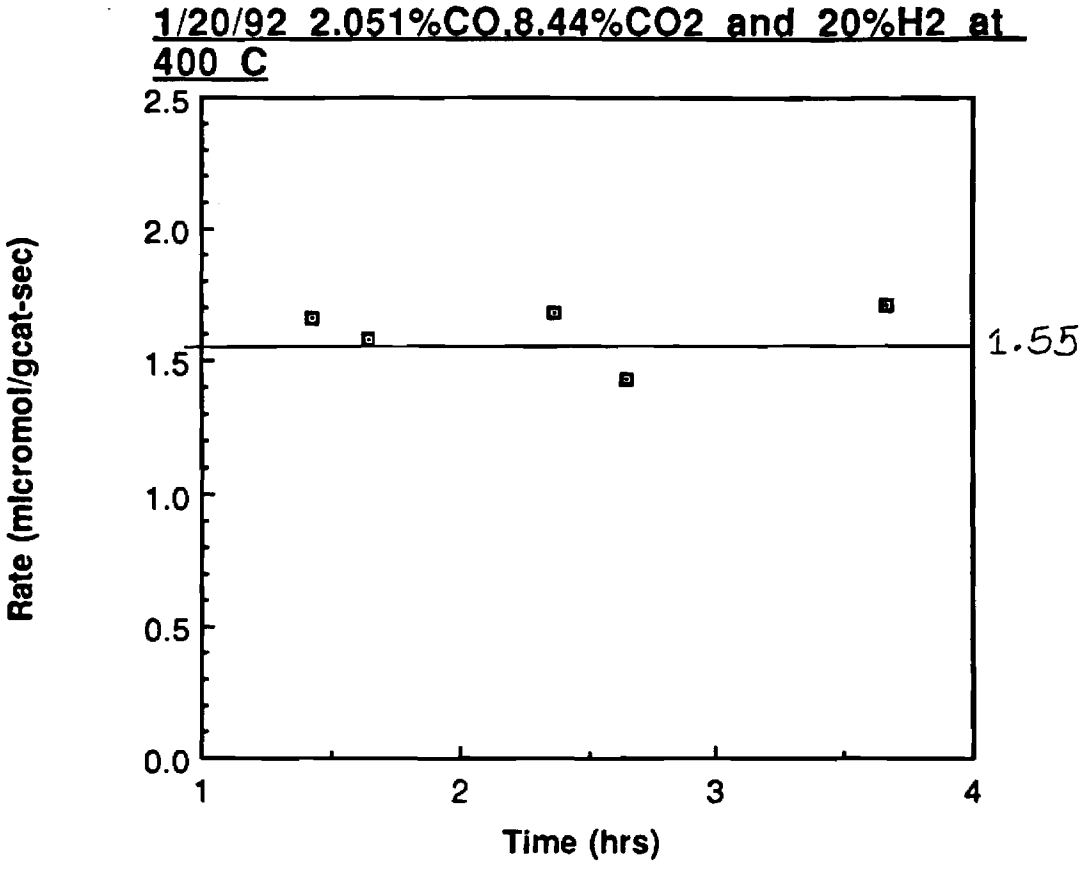
These data are being analyzed so that we can predict the external mass transfer coefficient (pertinent graphs are at the end of the report).

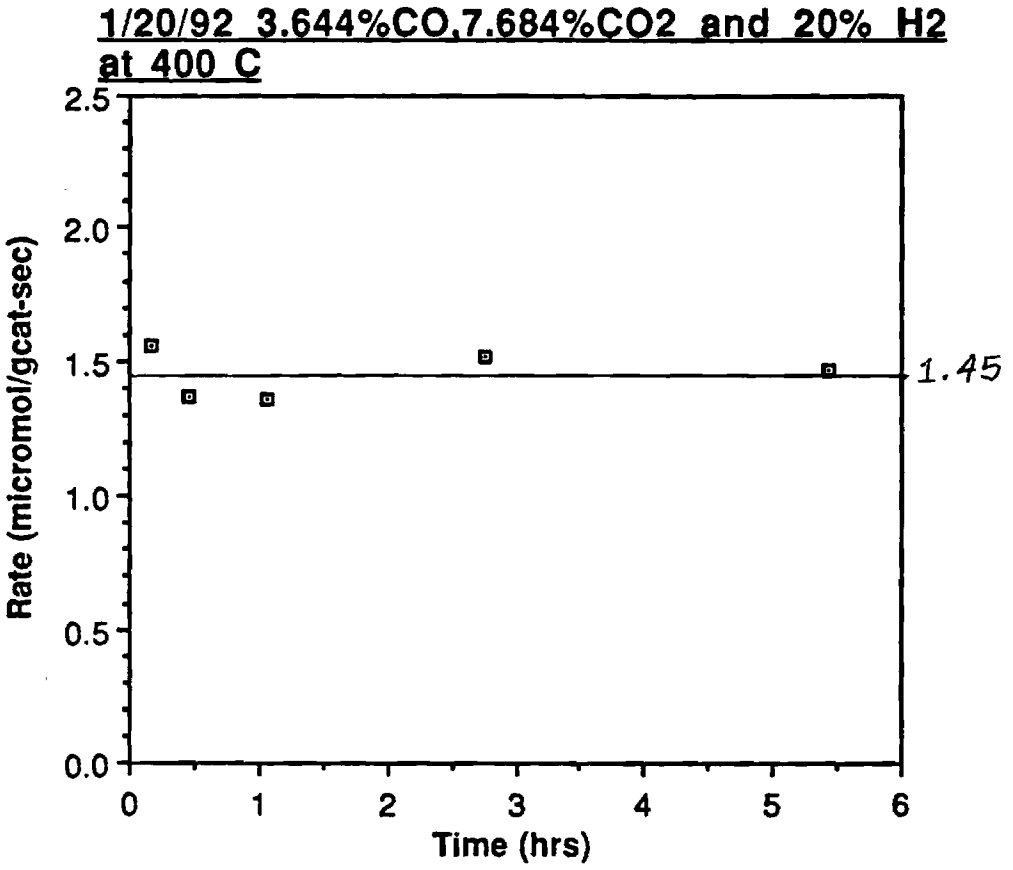
Presently work is being done to collect sample of the catalyst at different phase of transient studies to be analyzed by XRD and SEM.


1/16/92 9.22%CO2 and 20%H2 at 600 C
(homemade catalyst)
Rate (micromol/gcat-sec)
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100
Time (hrs)

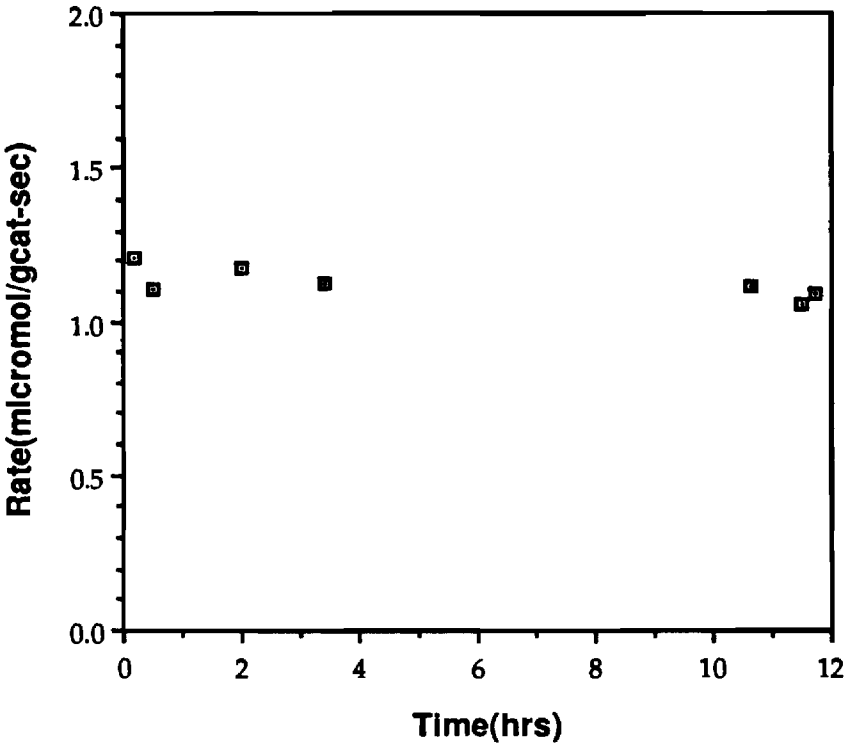
1/21/92 0.9658%CO,8.971%CO2 and 20%H2 at 400 C

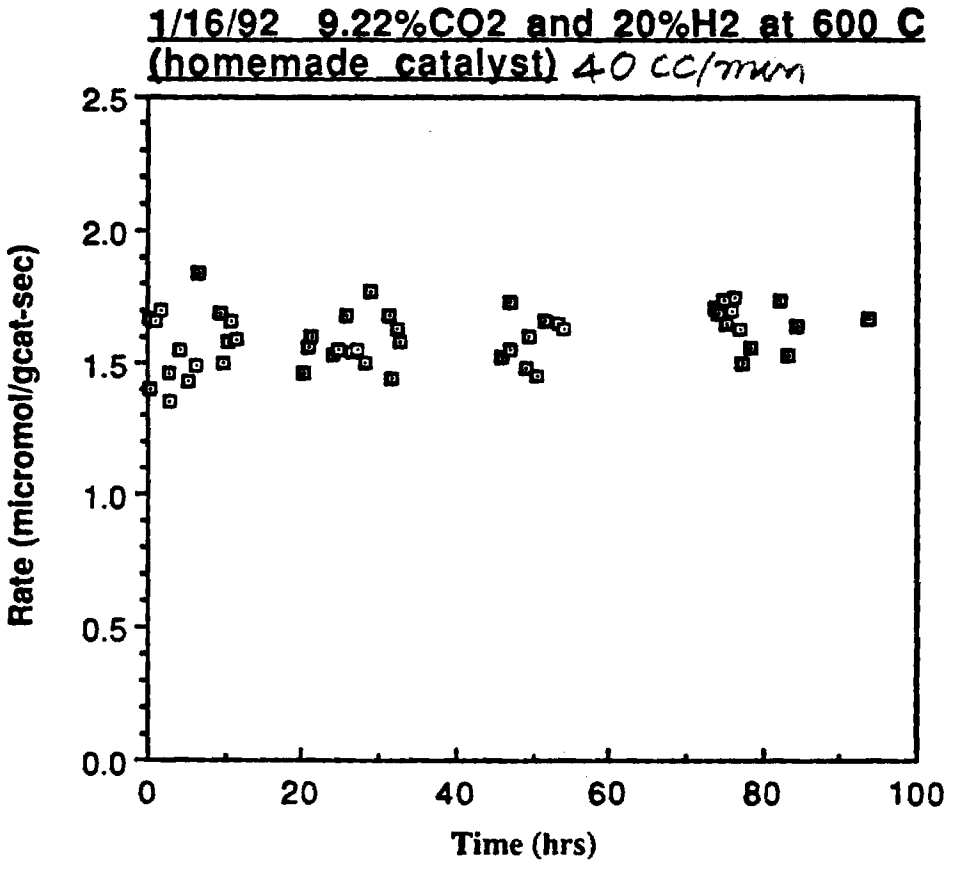



1/20/92 2.051%CO,8.44%CO2 and 20%H2 at 400 C
Rate (micromol/gcat-sec)
2.5
2.0
1.5
1.0
0.5
0.0
1
2
3
4
Time (hrs)
1.55


1/20/92 3.644%CO,7.684%CO2 and 20% H2 at 400 C
Rate (micromol/gcat-sec)
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
Time (hrs)
1.45

1/22/92 9.22%CO2 and 20%H2 at 600 C
Flow rate 20cc/min




1/16/92 9.22%CO2 and 20%H2 at 600 C
(homemade catalyst) 40 cc/mun
Rate (micromol/gcat-sec)
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100
Time (hrs)

1/21/92 9.22%CO2 and 20%H2 at 600 C
Flow rate 80cc/min